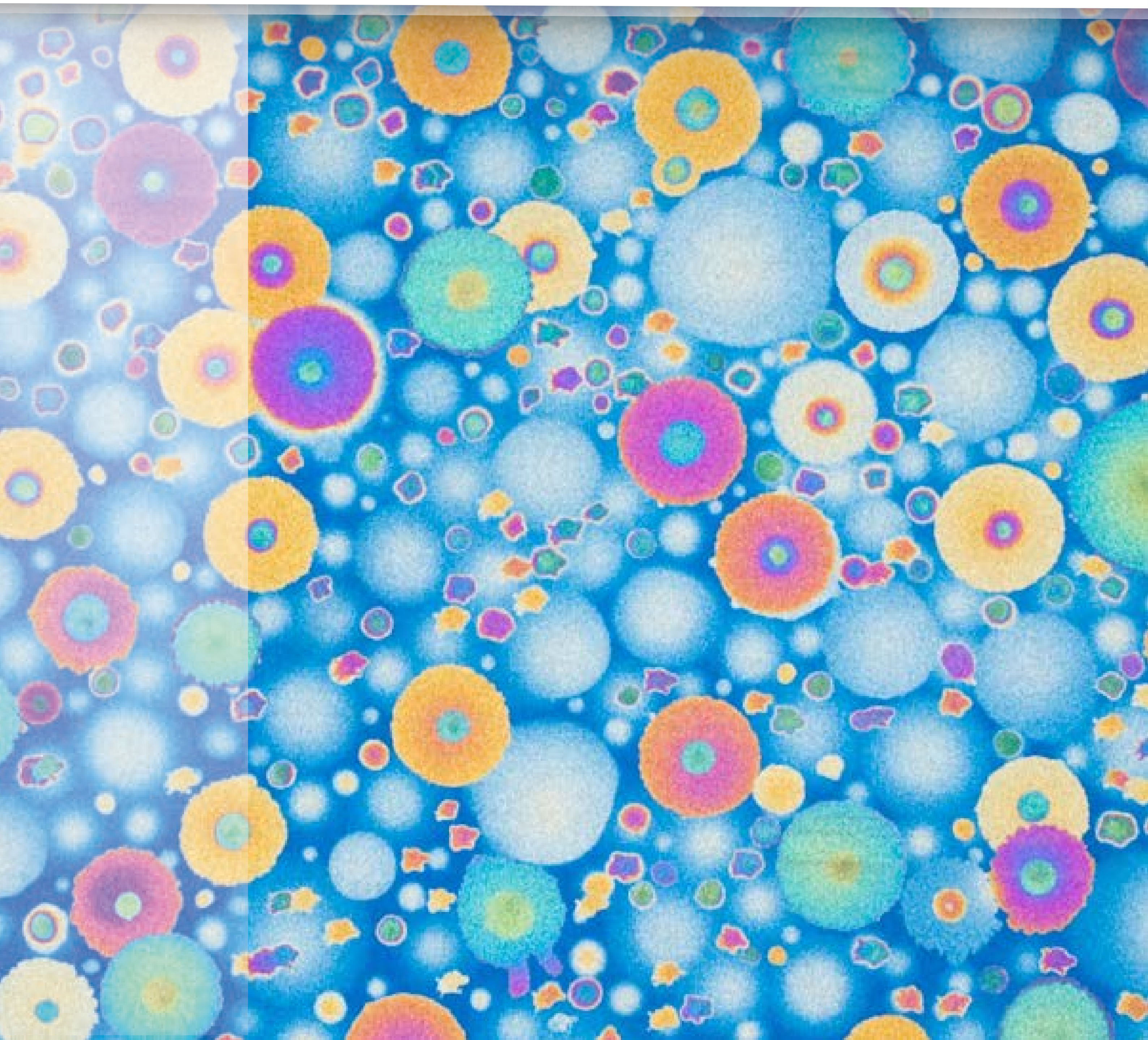
Pietro Pedeferri

Tales of corrosion (and other stories)



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Preface

This volume is a collection of some of the popular science publications, *Tales of Corrosion (Storie di Corrosione)*, written by Pietro Pedeferri over the course of his life. In these readings, corrosion is the *common thread* that connects his work as a scientist and engineer to that of a teacher and artist. The readings narrate episodes from his life, experiences related to his profession as a university professor and an expert in the durability of metallic materials, and his life as a titanium artist. The title echoes his book *Titaniocromie ed altre cose*, published by Interlinea in 1999.

The volume is divided into four thematic sections. The first section, dedicated to *Stories of the Science of Corrosion*, gathers readings dedicated to great scientists who have contributed to the understanding of corrosion mechanisms, laying the foundations of corrosion science and engineering. The narrative follows the lives of scientists starting from the late 1700s, particularly those with whom Pietro Pedeferri shared life paths. The second section, *Corrosion for Everyone*, collects some contributions published under the heading "corrosion notebooks" in the magazine *Pianeta Inossidabili*. Its ambition is to explain the fundamentals governing corrosion mechanisms in a simple yet rigorous manner and to elucidate the principal forms that characterize manifestation of this phenomenon. The third section, *Tales of Life and Corrosion,* narrates episodes from the author's life. Finally, the fourth and last section, *The Art of Corrosion*, is dedicated to the art that Pietro Pedeferri practiced with his Titaniocromie for over forty years. His activities as a scientist and artist are attested to by numerous awards, including the *Science pour l'art* award from the French Ministry of Culture and his membership in the Istituto Lombardo - Accademia di Scienze e Lettere. The readings collected here were published in the magazine *Pianeta Inossidabili*, edited by Valbruna, in the first edition of the book *Corrosione e protezione dei materiali metallici*, and in the magazine *l'Edilizia*.

MariaPia Pedeferri

Pietro Pedeferri

From Valtellina by birth, in Milan by adoption, with heart and spirit in Nestrelli.

Pietro Pedeferri (1938-2008) was born in Delebio (SO) and graduated in Chemical Engineering from the Politecnico di Milano in 1963. He became a full professor in 1983, first in "Electrochemistry" and later in "Corrosion and Materials Protection." He was a member of the Board of Directors and the Academic Senate of Politecnico di Milano. Additionally, he served as Head of Department and was a full member of the Lombard Institute Academy of Sciences and Letters starting in 2002.
He began his scientific activity in the field of electrochemistry. By the late '60s, he started focusing on the corrosion and protection of metals. This evolution, starting from general aspects, led him to become a leading figure in the field of active-passive material corrosion, bio-corrosion, cathodic protection of metallic structures, and corrosion and protection of reinforced concrete structures.

In this last field, in the 1990s, he conceived and developed a new method for preventing the corrosion of reinforced concrete structures at risk of chloride pollution, which he called "cathodic prevention." This method has been incorporated into the European standard EN ISO 12696 (Cathodic protection of steel in concrete), which includes diagrams bearing his name. The technique was applied in the restoration of the Sydney Opera House.

Pedeferri made significant scientific contributions to corrosion, both in terms of theoretical aspects and corrosion engineering. He authored highly regarded manuals that are used in both academia and industry.

From the late 1970s, he devoted himself with artistic sensitivity and scientific rigor to the oxidation of titanium, achieving extraordinary and surprising chromatic effects. His artistic endeavors in this field received various recognitions, the most prestigious being the award he received in Paris, alongside Mandelbrot, the mathematician known as the inventor of fractals, in the *Science pour l'art* competition of 1988.

He is the author of 33 books, particularly on the corrosion and protection of metals, cathodic protection, the durability of reinforced concrete, and the electrochemical coloring of titanium. He published over 380 research papers in scientific journals and conference proceedings, both nationally and internationally. A complete list of his publications is available at http://polilapp.chem.polimi.it

Table of Contents

Stories from the Science of Corrosion

Tribute to Volta

Though the battery was the most significant discovery of the scientist from Como, it was not his only one, since he also received recognition in the field of cathodic protection.

The second centenary of the invention of the battery was celebrated towards the end of the 20th century. Alessandro Volta wrote, "The great step that soon led me to the construction of the new shaking apparatus, which caused so much astonishment to all physicists and great satisfaction to myself, [happened] at the end of the year 1799." The invention took place in his hometown of Como, and not in Pavia, where Volta taught, because, with the return of the Austrians to Lombardy, the University was closed, and the professors, who had previously embraced the Cisalpine Republic and Napoleon's ideas, were sent home.

Within a few months, the availability of the new apparatus, capable of delivering a continuous current for hours or days, allowed for achievements and discoveries that were previously unimaginable. In London, Nicholson and Carlisle achieved the decomposition of water with the production of hydrogen and oxygen. In Pavia and almost simultaneously in London, Brugnatelli and Cruikshank carried out the first electroplating experiments: one with silver, mercury, and copper, the other with lead and copper. A few years later, Davy separated sodium and potassium from their molten hydroxides, and Berzelius produced chlorine and chlorates. In less than ten years, the foundations for the future electrochemical and electrometallurgical industry were laid.

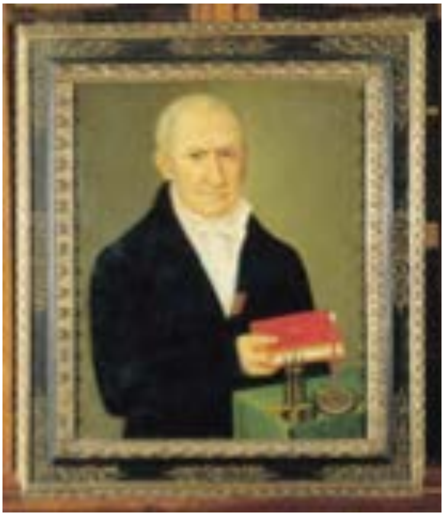
The column battery was created by Alessandro Volta by stacking discs of copper and zinc separated by an electrolyte made of a saline solution. The discs were soaked with fabric or other absorbent materials.

A series of completely incorrect predictions

Good boy but slow. Polvani writes, “Tradition has it that Volta had such a delayed and slow mental development as a child that there were fears he might remain mute. Nor did the concerns completely disappear when he still pronounced his first word at the age of four - a firm 'no' - because for a long time he struggled to speak, so much so that it took him three more years to have fluency in speech.”
I have read that even Einstein's family had fears that their son Albert was retarded, given the unusually long time it took him to learn to speak. Obviously, both of them made a remarkable recovery. They both became masters in the art of exposition. Imagine if Alessandro e Albert had had a normal mental development...

The sign of the evolution of means of production

But this was only the beginning, because the availability of the battery made the discoveries of Öersted (1819), Ampère (1820), and Faraday (1831) in electrodynamics and electromagnetismn possible, opening the door to 19th and 20th centuries science and technology of. Einstein said that all modern inventions have their roots in the invention of the battery. And he wasn't just thinking about inventions related to the world of electricity. However, even if we limit ourselves to



ALESSANDRO VOLTA

Como - February 18, 1745
Como - March 5, 1827

The photo shows the only portrait of the elderly Alessandro Volta (circa 1820), attributed to an anonymous painter. In the foreground, we can see a perpetual electrophorus and a model of a column battery, which were the first and last inventions “signed” by Volta.

this, the battery marked the beginning of the evolution of means of production and customs - and thus of society - towards the present, dominated precisely by electricity

It was, therefore, very fitting that, at the time, the image of Volta was featured on one of our most widely used banknotes (the 10,000 Italian Lire note) along with an illustration of one of his batteries. On the reverse side, there was an image of the Temple that Como had erected to honor its most illustrious citizen. It's also noteworthy that, in the year of the anniversary of this epochal event, the University of Pavia, the Politecnico di Milano, the Lombard Institute of Sciences and Letters, and other public and private institutions joined efforts to pay tribute to the scientist who made it all possible.

On a smaller scale, I like the idea of being able to contribute my own homage with this work.

To pay tribute to Volta, one could certainly discuss his inventions, with the battery being the most prominent but certainly not the only one. These inventions encompass the fields of electricity, as well as chemistry and physics, such as the discovery of methane or the determination of the laws of gas expansion.

Alternatively, one could elaborate on the numerous scientific controversies that Volta directly engaged in and won during his lifetime. We could start with the famous dispute with Galvani that captivated the entire scientific community in the last decade of the Enlightenment and divided it between supporters of the physics professor at the University of Pavia and the anatomy and surgery professor at the University of Bologna. We could end with the legacy he left concerning the seat of electromotive force, which engaged famous scientists for over a century – the likes of Ohm, Faraday, Joule, Maxwell, Helmolz, Gibbs, Lord Kelvin, Nernst, Poincare, Planck, and Einstein, to name just a few. This controversy, although somewhat dormant, has not been entirely resolved to this day.

In this controversy as well, which saw advocates of the chemical theory on one side and supporters of Volta's theory of contact on the other, Volta ultimately emerged as the winner. His approach now appears remarkably modern.

We could explain how and why some laws discovered or intuited by Volta were not directly attributed to him: for instance, the case of Ohm's law or the one known as Gay-Lussac's.

Alternatively, we could simply tell the story of the man: his upright and linear life, his travels, his relationships with the great figures of his time, starting with Napoleon, his romances, his beginnings as a poet, or his contribution to the cultivation and use of potatoes in Italy.

Since I cannot address all these topics, I choose to focus on one point within the theme I discuss on these pages, which is corrosion and the protection of metals. This is a point related to an important priority of Volta's remarkably overlooked, and which I reported in the "*Quaderni di Storia della Fisica*" in a paper titled "*Humphrey Davy, Alessandro Volta, and the Cathodic Protection.*"

Following the provisions contained in the Ministerial Decree of September 3, 1984, the Bank of Italy's Mint put into circulation the 10,000 Lire banknote dedicated to Alessandro Volta. On the obverse side, the master engraver Canfarini depicted the inventor of the battery and an example of it, of the "column" type. The reverse of the banknote, the work of engraver Zannotti, portrays the "Temple" in Como, dedicated to Volta and inaugurated in 1927 on the occasion of the first centenary of the illustrious citizen's death, along with the simultaneous opening of a major exhibition dedicated to him.

Rather harsh judgments

"He will dishonor the family and the homeland." In the summer of 1761, Volta spent his holidays in Gravedona, a village that overlooks the northernmost part of Lake Como. His friend Gattoni was with him. These holidays determined his future. To understand this, it is necessary to take a step back.

Volta grew up in a religious environment surrounded by religious figures: among his three paternal uncles, one was a canon, another an archdeacon, and the third a Dominican; the three older brothers were "already on the path to the sacred orders"; the school he had attended until that year was run by the Jesuits.

One of the professors, Father Gerolamo Bonesi, "had tried to draw him to the Company (likely referring to the Jesuits)," and probably the young Volta, initially, did not seem to be opposed to it.

But his uncle Alessandro, the canon - "who acted as a father to him since he had been orphaned, and who had been telling him since childhood that he wanted to make a good lawyer out of him" - upon learning of these *Jesuit intrigues*, had removed him from that school and, moreover, forbade him from approaching the Jesuit fathers.

It was during the summer holidays in Gravedona that Bonesi, despite the watchfulness of his uncle, continued his persuasive efforts, using Gattoni as an intermediary. Volta then realized that he had no vocation for the priesthood and confided this to his friend, who conveyed to Bonesi that "Volta has not the slightest idea of joining the Society."

The Jesuit priest, filled with vexation, then predicted that the future inventor of the battery "would lead a most wicked life, immersed in idleness and vice, to the great dishonor of his family and his homeland," and that his "dark" soul would end up in hell.

Whoever said that the language of the Jesuits is always ambiguous and nuanced! For the record, it should be added that Gattoni became a canon. Volta, in rebellion against his uncle's desire to make him a doctor of law, abandoned formal studies to dedicate himself to the "study of electricity," with "only books, his genius, and experiments as his teachers." For this reason, "neither then nor later did he ever attend university as a student, nor did he ever obtain a degree, not even an honorary one."

Regarding the hell evoked by the Jesuit priest, Volta "died with religious consolations" after uncertainties, doubts, and wavering in his faith. On the other hand, with six priests in the family...

History of science enthusiasts

First, I would like to mention two groups of history of science enthusiasts who, in my opinion, do not do justice to Volta.

The first group consists of those who attribute extremist opinions to the scientist from Como, which were not his own but rather those of his followers (they cannot be called students because Volta had none, just as he had no teachers). For example, regarding the aforementioned controversy about the location of the electromotive force, there are still those who write today that Volta believed it was localized only at the contact point between different metals and that the electrolytic conductor served only to allow the passage of current. Volta had refuted this idea on several occasions starting from 1796. To these individuals, it might be appropriate to recall the invitation that Volta extended to Nicholson, who had raised the same criticism. In essence, it can be summarized as follows: "Please, before saying what I think, read my papers."

Indeed, that is rather unrefined language

The second group consists of those who still believe today that the invention of the battery happened almost by accident or was a stroke of incredible luck. As one refined colleague put it (in a recent journal, it is described with more elegance as a discovery obtained "*by several strokes of very good fortune*" – several strokes, not just one, but the idea remains the same). Some even go as far as to say, as Ostwald did, that it resulted from an extremely fortunate mistake. Additionally, there are those who, regarding the theory that made it possible, continue to speak of an incorrect theory, or even a theory that caused a delay in the development of electrochemical thought.. Allow me to dedicate the following passage, written fifty years ago by Roberto Piontelli but still extremely relevant, to those individuals: "The path that Volta opened and followed in his experiments, leading him to decipher the intricate field of galvanism and to derive his marvelous invention, was not only the sole experimental approach of his time but also gains unique value in the light of modern methodology. Today, after more than a century and a half, we can assert that Volta's ideas, stripped of the extremism wrongly considered their essence, framed within the broader field of energetics, have more than ever the right to constitute a solid foundation for the theory of the battery."

Indeed, without any euphemism

"It lacks the logic of an observer." This point also helps to understand what happens when a university professor, including those of the highest reputation, speaks about a colleague.

Here, it is none other than Lazzaro Spallanzani, the renowned naturalist and professor, like Volta, at the University of Pavia, who is talking about Volta.

We are in 1794, and the controversy with Galvani had erupted a couple of years earlier. Spallanzani, often referred to as the *father* of artificial insemination, writes, "Today, Alessandro Volta has read a lengthy discourse against the electricity of Mr. Galvani. He relied on several of his own experiments, which, as is his custom, were immersed in a sea of words. I believe the spoken discourse will soon be published by him. It will be similar to his other memoirs. My worthy colleague has inventive spirit, but his head is full of fragile hypotheses, lacks the logic of an observer, and is verbose in presenting his ideas."

Certainly, if Volta had not lacked the logic of an observer...

Ironfoot

Humphry Davy and Cathodic Protection

Before returning to Volta, it is necessary to provide a context that takes us to London in 1823. In that year, the British Admiralty asked Sir Humphry Davy, the most illustrious scientist in Britain, to study the corrosion of the copper sheathing that covered the wooden hulls of ships of the time to protect them from the devastating action of shipworms. The following year, in front of the Royal Society of which he was president, Davy presented a paper that was immediately printed (*Philosophical Transactions*, 114, 1824) in which he announced the discovery of a new method to control corrosion based on coupling the metal to be protected with a less noble metal. In the paper, Davy demonstrates that copper in seawater becomes immune to corrosion when it is made slightly negative by connecting it to masses of iron or zinc. Davy recognized the practical importance of this discovery and proposed to the British Navy that they protect their ships in this way, or more precisely, the copper sheets that covered the wooden hulls of ships at that time.

The British Navy accepted the suggestion, and the following year, in 1825, they installed four elements (anodes, a term that would be coined by Faraday a few years later) made of cast iron and zinc on three ships. Specifically, cast iron anodes were mounted on the frigate HMS *Samarang*, which had just been launched, while zinc anodes were installed on the cargo ship *Carneba Castle* and on the yacht *Elisabeth* belonging to the Earl of Darley. The anodes on the latter ships ceased to function after a short time. However, the cast iron anodes installed on the HMS *Samarang* completely halted the corrosion of the copper sheets. Unfortunately, this also eliminated the toxic action of corrosion products on plant and animal organisms (*fouling*), which consequently thrived on the protected sheets. The frigate, which had already set sail from the port of Plymouth on its inaugural voyage to the East Indies, found itself unable to move easily off the coast of Portugal due to fouling. As a result, it had to make a stop in Lisbon to remove the anodes. Once the *Samarang* was lightened of the anodes and freed from fouling, it continued its journey to the East Indies.

The Admiralty decided to remove the new technique from the list of methods that could be employed for the protection of His Majesty's fleet.

Ironically, it could be said that Davy's protection technique had to be abandoned precisely because it worked. On the other hand, it's better to have a ship corroded but still able to reach its destination than one that doesn't corrode but then has difficulty moving. Unfortunately, as soon as the anodes were removed from the *Samarang*, the credibility of the new technique collapsed. It would take almost a century to recover it. Davy's confidence in a new success also waned. In fact, what is now considered one of his significant scientific contributions, the invention of cathodic protection, turned into a personal setback. The English scientific community criticized him.

HUMPHRY DAVY

Penzance - December 17, 1778
Geneva - May 29, 1829

An illustrious English scientist who became known for his experiments on the physiological effects of certain gases (one of which severely damaged his eyesight). He discovered, often with the assistance of his lab assistant, none other than Michael Faraday, six new chemical elements, including potassium and sodium.

Davy's bitterness is immense. He tries to understand why cathodic protection works in the laboratory but not in the sea. However, he cannot figure it out. Today, we know that zinc in seawater stops providing a current after some time if it contains iron impurities because it becomes passive. Evidently, the zinc used by Davy in the laboratory was purer than that installed on the ships. We also know that copper protected cathodically gets fouled due to the biological load present in natural seawater but not in the artificial and acidified water that Davy used for his experiments in London.

After this failure, Davy never fully recovers. In 1827, he is forced to resign from the presidency of the Royal Society. Although he is not yet 50 years old, he discontinues his scientific activity and leaves England. His health also deteriorates. At the beginning of 1829, in Rome, he experiences a first heart attack. He recovers within a few months and, in August, attempts to return to his homeland. He reaches Geneva, but there, he suffers a second heart attack and dies.

The most common quote attributed to Davy is the following: “The most important of my discoveries has been suggested to me by my failures.” Sadly, for him, the phrase could be reversed: “My greatest failure was produced by one of my great discoveries.”

It took nearly a century for cathodic protection, as the technique is known today, to regain credibility and be used again.

Nowadays, it is applied to prevent the corrosion of buried structures, pipelines, offshore platforms, reinforced concrete constructions contaminated with chlorides, ships, chemical and heat exchange equipment, and also to extend the service life of electric water heaters found in every household.

Stainless steels used in offshore applications are also cathodically protected to prevent localized attacks such as pitting and crevice corrosion. In many cases, this protection is achieved by coupling them with iron plates, much like the method used to protect the copper plates on the HMS *Samarang*.

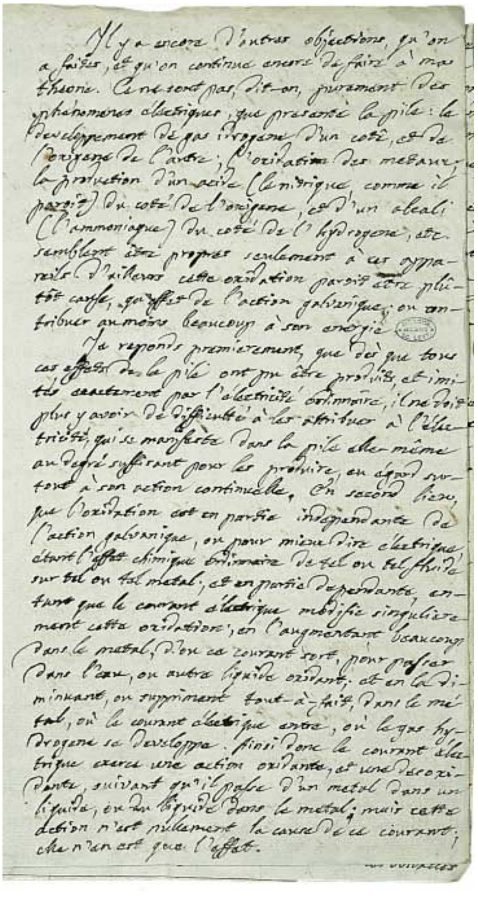
Scientific historiography rightfully acknowledges Davy as the first to propose the application of cathodic protection. Yes, he was. However, it also credits him with being the first to state the principle on which the technique is based, which is not accurate. The true priority belongs to Alessandro Volta.

This is the priority of Alessandro Volta

In a paper addressed to the editors of the Swiss journal *Bibliothèque Britannique* in 1802 and read *par l'auteur à la Societé de phisique e d'histoire naturelle de Geneve dan la séance du 27^e ventose* - Alessandro Volta writes: "*L'oxydation est en partie indépendante de l'action galvanique, ou pour mieux dire électrique; car elle est l'effet chimique ou ordinaire de tel ou fluide, sur tel ou tel métal; elle en dépend aussi en partie, en tant que le courant électrique modifie singulièrement cette oxydation, en l'augmentant beaucoup dans le métal d'où le courant sort pour passer dans l'eau ou tout autre liquide oxydant, et en le diminuant ou supprimant tout à fait dans le métal où le courant électrique entre, et où le gaz hydrogène se développe. Ainsi donc, le courant électrique exerce une action oxydante et une désoxydante, suivant qu'il passe d'un metal dans un liquid o du liquid dans le metal.*"

In these few lines, Volta makes three very important observations.

- First observation: First of all, Volta specifies that "oxidation is partly independent of galvanic or, more precisely, electrical action, because it is the usual chemical effect of one or the other agent on this or that metal; it partly depends on this action because the electrical current uniquely modifies this oxidation." Nobody before him had explained the corrosive phenomenon and the corrosion rate in terms of local corrosion and oxidation due to external polarization in such clear and correct terms. Naturally, Volta does not understand that corrosion is an electrochemical phenomenon, even though he states that the exchange of current between the metal and the solution can accelerate or inhibit corrosion, depending on whether it occurs in one direction or the other. The hypothesis of the electrochemical mechanism of corrosion phenomena would indeed be advanced by De la Rive only in 1830. The concepts expressed by Volta in 1802 will find a complete framework only in our century, in the period between the two world wars, when the Cambridge school (Hoar, Mears, and Brown) developed the theory of cathodic protection, and the German school in Munich (Wagner and Traud) developed the theory of mixed potentials.



Il y a encore d'autres objections, qu'on a faites, et qu'on continue encore de faire à ma théorie. Ce ne sont pas, dit-on, purement des phénomènes électriques, que présente la pile: le développement de gaz hidrogène d'un côté, et de l'oxigène de l'autre; l'oxidation des métaux; la production d'un acide (le nitrique, comme il paroît) du côté de l'oxigène, et d'un alcali (l'ammoniaque) du côté de l'hydrogène, etc. semblent être propres seulement à ces appareils. D'ailleurs cette oxidation paroît être plutôt cause, qu'effet de l'action galvanique, ou contribuer au moins beaucoup à son énergie.

Je réponds premièrement, que dès que tous ces effets de la pile ont pu être produits, et imités exactement par l'électricité ordinaire, il ne doit plus y avoir de difficulté à les attribuer à l'électricité, qui se manifeste dans la pile elle-même au degré suffisant pour les produire, eu égard surtout à son action continuelle. En second lieu, que l'oxidation est en partie indépendante de l'action galvanique, ou pour mieux dire électrique, étant l'effet chimique ordinaire de tel ou tel fluide sur tel ou tel métal, et en partie dépendante, en tant que le courant électrique modifie singulièrement cette oxidation, en l'augmentant beaucoup dans le métal, d'où ce courant sort, pour passer dans l'eau, ou autre liquide oxidant, et en la diminuant, ou supprimant tout-à-fait, dans le métal, où le courant électrique entre, où le gaz hydrogène se développe. Ainsi donc le courant électrique exerce une action oxidante, et une désoxidante, suivant qu'il passe d'un métal dans un liquide, ou du liquide dans le métal; mais cette action n'est nullement la cause de ce courant, elle n'en est que l'effet.

The excerpt from Alessandro Volta's 1802 letter to the editors of the "Bibliothèque Britannique" outlines the principles underlying cathodic protection (Cartellario Voltiano, segnatura L 26 presso l'Istituto Lombardo Accademia di Scienze e Lettere di Milano).

Pietro Pedeferri was a corresponding member and later a full member of the Lombard Institute of Sciences and Letters from 2002 to 2008.

- Second observation. Volta notes that "oxidation increases significantly on the metal from which the current exits to enter the water or any other oxidizing liquid." This behavior had already been observed before the invention of the voltaic pile, by Giovanni Fabbroni, and immediately after his invention, by Nicholson, Davy, and Wollaston. In a letter dated September 22, 1800, to his friend Landriani, Volta writes that the previous April, he had noticed, in addition to the development of hydrogen and oxygen, "the calcination of metals and especially of zinc." What is the novelty then? It is that until 1802, the corrosion occurring on the metal from which the current exits was believed to be solely due to the exchanged current, whereas, as stated by Volta, it was also due in part to localized corrosion processes..
- Third observation. Now we come to the most important point. "Oxidation," Volta emphasizes, "decreases or is completely eliminated on the metal where the current enters and where hydrogen is generated." But this is cathodic protection! So, in 1802, not in 1824, Volta was the first to understand the principles governing this technique and to describe its effects, including side effects such as the development of hydrogen.

Today, every cathodic protection specialist knows that when steel, or any other more noble metal like tin, nickel, or copper, is polarized to the point where hydrogen is generated at its surface, corrosion ceases. Volta had already understood this in 1802.

Napoleon, Volta e Voltaire: the game of the three letters

Napoleon had great respect for the inventor of the battery. He proposed medals, recognitions, honors, and political positions for him. When Volta presented the battery to the members of the Institute of France in 1801, during three separate meetings of the Institute, Napoleon didn't miss a word.

Volta wrote to his wife a few days after the first meeting: "Bonaparte told me many gracious things when we first met, and (having learned) that the next day I was to read a paper at the same Institute, he then told me he would attend. Indeed, he came in his capacity as a member of the Institute, standing in line with the President Haüy and Mr. La Place, who is also a Senator. I was called to stand in front of him to deliver my reading (...). He interjected several times with questions, and when I finished reading, Bonaparte took the floor and praised my discoveries, suggesting that the Institute should award me the gold medal and invited me to continue experiments with those of them more dedicated to Physics and Chemistry, allowing me to conduct experiments on a larger scale and at any expense. He went into detail, suggesting perspectives regarding the different compositions of metals, which determine galvanic effects (...) specifically the transition of the same metal from one state to another, notably the transformation of iron from cast iron to softer malleable iron, steel, etc.”.

In short, an electrochemical and metallurgical Napoleon.

There's a curious anecdote, reported by Victor Hugo, that highlights Napoleon's respect for the inventor of the battery and perhaps even more so, his dislike for the author of “Candide”. In 1803, while visiting the library of the National Institute, Napoleon stopped in front of a plaque with a golden wreath and the inscription “To the great Voltaire”. Napoleon, turning to his entourage, ordered the last three letters to be erased.

Giovanni Fabbroni

Giovanni Fabbroni was a prominent figure on the Florentine cultural scene during the late 18th and early 19th centuries. For many years he served as the vice-director of the Imperial Regio Museo di Fisica e di Storia Naturale in Florence and was a driving force in the city's cultural life. He had diverse interests, ranging from economics, chemistry, agrarian studies, to law. In 1792, he presented a paper to the Accademia dei Georgofili on the interaction of metals when coupled together. The paper, which was not immediately published but only in 1799 in the *Journal de Physique* (49, 348, 1799) under the title *Sur l'action chimique des différent métaux entr'eux, à la température commune de l'atmosphère; et sur l'explication de quelques phénomènes galvaniques*, is of great significance. Piontelli wrote that with this work, Fabbroni "establishes the chemical theory of galvanism and lays the foundation for the galvanic theory of corrosion a decade before Volta's invention."

This paper is primarily the result of keen observations. For instance, Fabbroni writes, "I have observed that the alloys used to solder the copper plates on the movable roof of the Florence Observatory have rapidly transformed, altered into white oxide, right at the points of contact with the copper plates. I have also learned that iron nails used to fasten copper sheets to the hulls of ships rust so much that their stems swell to the point of exceeding the dimensions of their heads.

This is also the result of a series of intelligent experiments, such as the following: "In one container filled with water, I placed small gold foils, in another silver, in a third copper, and then in others, tin, lead, and so on. In other glasses, I placed the same metals in pairs, one more oxidizable than the other, separated by a small glass blade. Finally, in a third series of glasses, I put the same metal pairs in direct contact with each other. The first two series showed no changes, while in the third, the more oxidizable metal visibly transformed into oxide immediately after coming into contact with the other metal, and the oxide gradually increased. This phenomenon began, even if imperceptibly, at the same moment of contact [...] but after a month, I observed that several metals not only turned into oxide but also formed small salt crystals of different shapes on their surfaces. It seemed to me that a chemical action [between the metals] had clearly taken place.”

Fabbroni's experiments and observations were crucial in understanding the chemical interactions between different metals and laid the foundation for the development of galvanic and corrosion theories.

And further on, he reiterates: “It seems to me that from these and other observations, one should acknowledge that metals in these cases exert a mutual action that is the cause of the phenomena that occur following their junction or when they come into contact.”

In the past, scientists' opinions on these passages were contradictory. Some recognized in Fabbroni's observations on the corrosion of metals in contact the embryo of the chemical theory of the cell, while others even ignored the fact that they clearly mark the beginning of the correlations between galvanism and corrosion phenomena. Today, no one doubts anymore that the publication of this paper was a significant scientific event.

P.S. The beautiful Museum of the History of Science in Florence, which was previously to the museum where Fabbroni worked, dedicates an entire room to its former vice-director but does not mention his important contribution. We hope they will rectify this in the future..

GIOVANNI FABBRONI

Firenze (Florence) - February 13, 1752
Pisa - December 17, 1822

Luigi Valentino Brugnatelli

Luigi Brugnatelli (1761-1818) was born in Pavia. He graduated from the University of Pavia in 1784 and taught chemistry there from 1786 until his death. Alessandro Volta, who had been his student, found in him a valuable collaborator and frequently visited his laboratory. A few months after the invention of the voltaic pile, Brugnatelli conducted pioneering experiments in electroplating metals, likely predating similar, independent work by Cruikshank in London. Brugnatelli successfully deposited silver, zinc, mercury, and copper using his method.

These early experiments led to further endeavors aimed explicitly at obtaining metal deposits and coatings. In 1802, using his ammonium-based method, he deposited various metals, including gold. In 1805, he published a work titled *Maniera di indorare le medaglie, e i fini pezzi di argento con il galvanismo* (How to Gild Medals and Fine Silver Pieces with Galvanism). Brugnatelli recognized the industrial potential of the process and shared it with a goldsmith in Pavia, who put it to use.

In 1816, he achieved the galvanic metallization of carbons, particularly using copper sulfate bath, and in 1818, he deposited alloys through displacement with zinc. Unfortunately, these experiments were not widely known at the time, and more than

LUIGI VALENTINO BRUGNATELLI

Pavia - February 14, 1761
Pavia - October 24, 1818

A scientist from Pavia who promoted the development of galvanics. He unsuccessfully proposed changing the name of the element nitrogen to “fossigeno” (generator of light) and later to “septone” (putrid).

three decades later, their repetition appeared as a new discovery, bringing fame, honors, and glory to others.

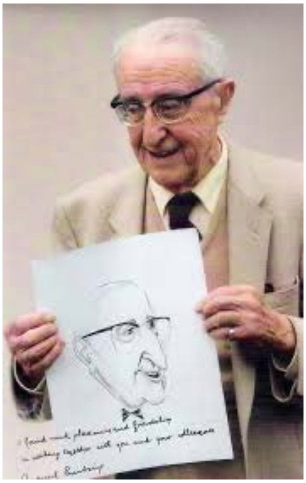
Brugnatelli's scientific contribution to the birth of galvanism, although greatly facilitated by his association with Volta, was significant. The fact that his work received little recognition in international scientific circles is likely due to the discredit he faced as a result of his unsuccessful attempts to reform chemical terminology and his imaginative ideas, particularly concerning electric fluid. Additionally, unlike someone like Davy, who was active during the same period, Brugnatelli couldn't provide a coherent explanation for the complex phenomena he observed. Furthermore, most of his work was published in Italian journals that he himself founded, such as the *Annali di Chimica, Fisica, e Storia Naturale* or the *Giornale di Fisica, Chimica, Storia Naturale ed Arti*.

His influence in Italy is distinct. The spread of galvanic art that emerged in our country in the early decades of the century is primarily his merit. In Pavia, his experiments in metal electrodeposition enabled the city's goldsmiths to be the first to use this technique. In Venice, his pupil, Marianini, became a pioneer in the field of galvanoplastics (ahead of Jacobi) and in 1840 published the *method for obtaining bas-reliefs in copper*. In Venice once more, Zantedeschi, one of the early enthusiasts of electrotyping, published a treatise on this technique in 1841. In 1826, Leopoldo Nobili discovered the coloring of metals by anodic oxidation in Reggio Emilia. In Modena, Grimelli, with the goal of making use of the copious precipitate of insoluble gold ammonium obtained by following the Brugnatelli method, used an aqueous solution of potassium cyanide. Selmi (1817-46), who made significant contributions to electroplating, published the first Italian manual of galvanic art titled *Manuale dell'arte d'indorare e d'inargentare con metodi elettrochimici e con la semplice immersione* (Manual of Gilding and Silvering with Electrochemical Methods and Simple Immersion) in 1844. The field developed to the extent that by 1844 Grimelli could publish a scientific and artistic history of Italian original electrometallurgy.

Marcel Pourbaix

Marcel Pourbaix played an important role in the field of corrosion. For nearly forty years, starting from when he presented his thesis in 1945 titled *Thermodynamics of Dilute Aqueous Solutions. Representation of the Role of pH and Potential*, he was part of a group of scientists who, following in the footsteps of Evans, contributed to the development of the science of corrosion based on thermodynamics and electrochemical kinetics. They worked to bridge the gap between the world where corrosion occurs and is countered with that of experimental research and theoretical speculation.

He also worked as an educator along this line. Speaking specifically about the teaching of corrosion (although his statement could apply to other courses), he wrote: "Only those who know, can do, and do - in other words, only those who understand the fundamentals of corrosive phenomena, have replicated and studied them in the laboratory, and have fought against them in the field - are capable of imparting knowledge about corrosion, in other words, they are able to teach it effectively". Unfortunately, in some places, there is a saying, "Those who can do, do, and those who cannot do, teach," which advocates the opposite approach.



MARCEL POURBAIX

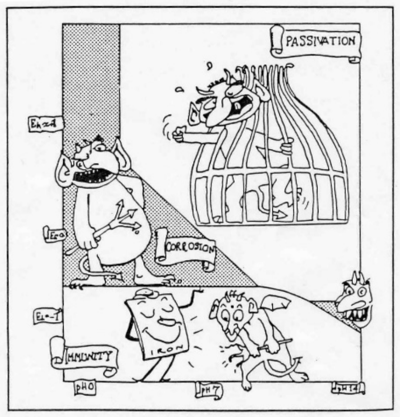
Myshega - September 16, 1904
Uccle - September 28, 1998

Conducted his well-known studies on corrosion at the University of Brussels, where he developed the diagrams that bear his name.

In 1990, during the eleventh World Corrosion Congress in Florence, in recognition of his merits, he was awarded a decorated titanium plate with the title *Interpretation of the Chromatic Aspects of Passivation Phenomena and Passive Conditions*. The author of this work spent a week preparing it. Later on, in 1992, Alex Pearson featured a cartoon in the Electrochimica Acta dedicated to him.

But let's return to his thesis. Pourbaix initially submitted it in 1940. Those who were supposed to judge it didn't grasp its importance, and the discussion was postponed, possibly due in part to the war that had just begun. As a result, the thesis could only be defended after the conflict ended in 1945. The initial rejection did not prevent his diagrams from becoming, as some have called them, the "Rosetta Stone" for understanding passivity phenomena, and Pourbaix himself became one of the leading scientists interested in corrosion.

(Interestingly, even eighty years earlier, Arrhenius's thesis on the hypothesis of the electrolytic dissociation of saline solutions was rejected. In that case as well, the unpromising graduate's career was not halted; quite the opposite. Evidently, rejections in the fields of corrosion and electrochemistry are a good omen. So, if a student finds themselves retaking the corrosion exam multiple times, they shouldn't worry. If they are compelled to do so, it might be to allow for a brilliant career, at least as brilliant as that of Pourbaix or Arrhenius.)



Pourbaix diagram of iron by Alex Pearson (from Electrochimica Acta, 1992).

Roberto Piontelli

Professor Piontelli was an internationally renowned scholar. During the war years and in the immediate aftermath, he laid the foundations of modern electrochemistry. In 1949, along with leading European and American figures in this field, he co-founded CITCE, the International Society of Electrochemistry, which continues to operate today, albeit under a different name. The electrochemistry he encountered as a recent graduate in the early 1930s was focused on "fundamental issues concerning the thermodynamics of charged species" and conventions – of signs, among other things – "that allowed for writing numbers but left the underlying principles in obscurity". It was an electrochemistry that had marginalized fundamental problems in favor of a focus on the theory of solutions and electroanalytical techniques. In contrast, what he faced fifteen years later was an electrochemistry "renewed, simplified, formally aligned with other disciplines, ready for the developments of the following years, and capable of assuming the interdisciplinary role that befits it".

Piontelli made a significant contribution to this transformation. He established the discipline on a chemical-physical foundation and perfected its experimental methods.

Thus, when he returned to the Politecnico in 1948 as the director of the institute

ROBERTO PIONTELLI

Lodi - May 11, 1909
Milan - October 15, 1971

from which he had been expelled twelve years earlier, he was ready to take new steps forward. On the experimental front, he investigated the anodic and cathodic behavior of polycrystalline and monocrystalline metals, delved into issues and aspects of their corrosion and protection, and engaged in the field of electrometallurgical applications in aqueous solutions or molten salts. On the theoretical front, he made significant contributions to the understanding of thermodynamics and electrochemical kinetics, the theory of the galvanic cell, and wet corrosion processes. Piontelli also made a significant methodological contribution to research in this field. His philosophy is essentially Baconian. He writes, paraphrasing the English philosopher, "only the activity of the bee is suitable for electrochemistry". In this discipline, *ants* are not needed, that is, experimenters who *collect* and *use the results* of their measurements without caring to understand what happens in their systems. *Spiders* are not needed either, that is, scholars who *construct their own theories* – "they weave their webs by themselves" – without deigning to know the reality. *Bees* are what is needed; they *suck nectar* from the flowers in gardens and fields and then process it to transform it into honey. In a cross-disciplinary field like electrochemistry, and perhaps even more so in corrosion, only on a solid phenomenological foundation can both the tower of the most daring theoretical speculation and the most modest but robust and efficient structure of rational technology be built.

Piontelli embodies the qualities of a scholar in the field of electrochemistry who pays careful attention to integrate its various aspects, including those related to corrosion, into the broader context of physical chemistry. He is both an experimenter at the forefront of research and a technologist who understands industrial processes and their corrosion implications. He is also a historian who has studied the origins and developments of this field, and a teacher in an engineering faculty. This unique combination places him in the best position to bridge the gap between the "ants" working in the world of industry and applications who may not understand what happens in their cells and the "spiders" usually nested in academies who often lack knowledge of both the production world and practical applications. This position also enables him to transfer knowledge and methodologies from the laboratory to the factory and to integrate *field experience* into research. He operates in this way. First and foremost, he constructs a mosaic of the electrochemical behavior of metals, generalizing the results of observations, calculations, studies, and contemplations. He recognizes essential factors and the relationships that bind them together and frames them within a broader rational context. Then, in the laboratory, he analyzes specific industrial processes or corrosive phenomena with the aim of rationalizing them and creating methods and tools to improve one and counteract the other. In all cases, he follows "the essential criterion that a small contribution to a significant problem is preferable to the most complete success in answering an isolated question." Next, he delves into specific issues in industry and electrochemical applications. Convinced that, in fields like these, which "were born from empiricism and often remain devoted subjects to it," the solution to fundamental problems should be based on *chemical-physical and theoretical premises*, he works to transform the dominant technology based on experience and common sense into *rational technology*. Finally, closing the cycle, he draws suggestions or inspiration from industrial reality to reorient his teaching and research work. Among his books, I recall the volume *Elementi della teoria della corrosione a umido dei materiali metallici* (E. Longanesi, 1961), which is the first significant Italian book on this subject: beautiful but challenging to understand.

The character

For us young assistants, Professor Piontelli was a charismatic figure. We considered him to be the greatest Italian electrochemist after Volta. We admired him for his extensive knowledge of physical chemistry, his extraordinary work ethic, the creativity of his theoretical approaches, his lectures, and his writings. What fascinated us was that, bypassing all intermediate hierarchies, he would directly inquire about the progress of our research and engage in discussions with us about the results and plan the work. When he was in the mood, which was often, he did it with joy and irony, elaborating on his thoughts about the research with Latin quotations, jokes in

The roster of A.S. Fanfulla 1925-1926 in which Piontelli was a player.

dialect, idioms from soccer slang, and Milanese proverbs. And he managed to make any work we were doing seem essential. Adding to the legendary aura around his figure was another factor. He had played as a right-back in Fanfulla of Lodi soccer Team before moving to Ambrosiana, where, in the first league match, an ankle injury had ended his soccer career. (To be honest, besides the accident, it seems that Giulio Natta, his teacher and friend, also played a decisive role, telling him, "You must choose: either soccer or the Politecnico.") He was immensely wealthy, to the point that every year when the Corriere published the list of the top Milanese taxpayers, we checked to see if he had moved up or down in the top ten rankings. He had a library of books, codices, and ancient documents - some of which belonged to important scientists from past centuries - befitting a Renaissance prince. At 17, he obtained a classical high school diploma, at 22 an engineering degree, and at just over 30, he won a professorship.

In 1958, some colleagues from CITCE, through their respective national academies, had nominated him for the 1959 Nobel Prize in Chemistry. Persistent rumors had suggested that the Nobel would go to a European electrochemist. However, when a prominent member of the Royal Swedish Academy of Sciences asked to come to Milan to meet him, Piontelli scheduled an appointment but did not attend the meeting, almost intentionally compromising that nomination. The Nobel Prize went to another electrochemist, the Czechoslovakian Heyrovsky.

We soon became aware of his flaws as well. We witnessed his daily conflict-ridden relationships with the students who had left him to secure a position offering a decent salary; his bitter criticisms of the few assistants who had entered academia without his support or assistance. He frequently launched snide comments at this or that collaborator for trivial reasons, and his sudden outbursts towards academic figures or personalities were not uncommon. He was suspicious and distrustful even of those closest to him, as if he feared betrayal.

In the academic environment where he was highly regarded, he had only a small circle of friends and made no effort to win over the others, even if they were prominent scientists. For example, when offered membership in the Accademia dei Lincei, he responded with a brief and certainly not endearing note: "I do not want to appear even as an extra on the stage where the giants of Italian science are performing." A few years later, evidently, he changed his mind since he accepted co-optation into that prestigious institution.

The same held true more or less at the international level. In the CITCE, alongside some friends, there were scholars he simply could not stand. For example, he seized every opportunity to attack Bockris, a very famous electrochemist of those years. One day, a colleague from Padua commented: "I'm worth a ten, you're worth a hundred, but let those worth ninety-five live as well."

In short, he had a bad temper and he didn't hide it, even though he was a shy man.

As unconventional as he was in his research, he was a conservative in politics. It bothered him that there might be communists in his institute. At one point, he even believed in the presence of KGB-paid spies. He believed he was a perfect liberal. Yet, he did not admit individuals with ideological and cultural positions different from his own among his collaborators, nor did he tolerate union demands.

In his life and manners he was also old-fashioned. In fact, to put it bluntly, today we would consider him a killjoy. Once, when examining candidates for a secretarial position at his institute, the only selection criterion he proposed to the evaluation committee was: "We do not want Miss Italy." Fortunately, the shy eighteen-year-old who showed up for the tests had the insight or cunning to hide her charms - which she would reveal later - under a black apron. She was hired.

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Giuseppe Bianchi

Giuseppe Bianchi earned his degrees at the Politecnico di Milano, first in chemical engineering and later in electrical engineering. He began his teaching and scientific career there in 1943. In 1959, he was called to the University of Milan, where he held the chair of Electrochemistry for more than thirty years and established the Institute of Electrochemistry and Metallurgy, eventually making it one of the leading research centers in Europe in the field of electrochemistry and corrosion.

He was a man of high culture and moral stature, a great researcher, and a skilled anti-corrosion technician, and he can be considered the first true corrosion scientist in Italy. This last vocation was always present in his work but became predominant from the 1980s onwards when he first addressed the problem of plant reliability in relation to the risk of corrosion and later tackled the transfer of his corrosion experience to emerging expert systems.

He was also a great teacher. His lectures fascinated generations of students, researchers, and technicians. I had the great fortune of attending his courses and seminars as a graduate student, along with those of three other formidable masters: Piontelli, who gave excellent but sometimes challenging lectures (when the rigor of

GIUSEPPE BIANCHI

Bergamo - November 13, 1919
Bergamo - August 21, 1996

his exposition led him to add a third or fourth index around a symbol, he would sometimes jest about it: "One must be clear," and he meant to say rigorous, "even at the cost of not being fully understood." T.P. Hoar was intelligent and full of humor, and finally, N.D. Green who could effectively convey the culture of the Fontana school of American thought and his experience as an industrial consultant in a simple manner. While not taking anything away from the value of the other three masters, Bianchi was the teacher I loved most due to his extraordinary ability to communicate with audiences of any level. His humanity, culture, wit, and enthusiasm made him a remarkable professor.

His great teaching ability is also evident in his book on corrosion (written with Francesco Mazza) and his splendid monographs, from the one on cathodic protection, awarded by the Ministry of Industry in 1954, to those on corrosion and protection in the cooling circuits of thermal or nuclear power plants in the 1970s. In these works, his perfect knowledge of electrochemistry and the operational behavior of materials allows him to rationalize very complex corrosion processes and, therefore to predict and control them.

Perhaps he was such a complete teacher because he always knew how to put himself in the position of someone who has to learn from others. I myself remember him with pride and sympathy as a diligent and curious student, sitting in the front row, in several courses held in the 1980s at the Politecnico on cathodic protection or corrosion in concrete. I also recall him as a classmate - when he was already in his seventies - during refresher courses on expert systems. He followed these with the same attention he had always paid to students reporting research results or to technicians describing corrosion cases. He would then offer advice or recommendations to both, even when they didn't explicitly request them. It was this openness that truly made him the patriarch of the corrosion community, as he liked to call himself.

U.R. Evans and T.P. Hoar

The credit for advancing the hypothesis that corrosion occurs through an electrochemical mechanism is generally attributed to De La Rive, around 1830. However, in reality, it was Evans who, almost a century later, demonstrated it and introduced electrochemical methodologies into the study of these phenomena, including the diagrams described in this chapter bearing his name.

I was fortunate to meet this scientist in 1972 during my stay at the Department of Metallurgy at the University of Cambridge. He had already been retired for some time, but he still visited his old laboratory at least a couple of times a year. I still remember the excitement that these visits generated among all of us researchers..

His scientific merits are part of the history of corrosion. Here, I would like to recall just one episode that allows us to outline his human character. In 1970, a student (who is now Professor Luciano Lazzari) asked his colleague Bruno Mazza to help him find a foreign university laboratory where he could avail himself of a scholarship provided by their Pavese college, Ghislieri. Bruno thought of Evans, whom he knew by reputation, and wrote to him, knowing that he was still active despite being nearly eighty years old. In a swift exchange of letters, Evans replied that he would be very happy to welcome the student to his laboratory. In fact, he contacted the student

ULICK RICHARDSON EVANS

Wimbledon, London - March 31, 1889
Cambridge - April 3, 1980

directly, arranged for his visit, and scheduled a meeting at the bus station in Cambridge. The student departed with a bit of concern since he didn't know how he would recognize the scientist in a place he assumed would be very crowded. However, as soon as he got off the bus, he saw a sprightly octogenarian, tall and distinguished, holding a large sign that clearly read EVANS. After being recognized, the student was first taken to King's College, where Evans was a *fellow*, and had the honor, reserved only for esteemed guests, of strolling on the lawn. Later, they visited Evans' home for a cup of tea. (Can you imagine a local professor at the central station patiently waiting with a sign for an Erasmus student, then taking them for a stroll in the Politecnico gardens and, in the end, inviting them to his home for coffee?).

While at Cambridge, I had the opportunity to associate with another distinguished scientist, T.P. Hoar, who hosted me in his laboratory for almost a year. He had inherited the laboratory from his mentor, Evans, along with the position of *Reader in Corrosion and Protection* within the university. (It seems impossible, but neither of them ever became a *Professor*.) He, too, had made significant contributions to the development of our field, and his name was well-known both inside and outside the academic world. The year before, for instance, he had produced an important document on the costs of corrosion for Her Majesty's Ministry of Industry, famously known as the "Hoar Report," still cited today.

Five of us shared the few square meters of the historic laboratory: four doctoral students, all nearing their PhDs, hailing from Scotland, Argentina, Ceylon, and New Zealand an myself. They were a few years younger than me. T.P. Hoar, Sam – as we called him – was close to retirement. He had always been a theater enthusiast but had recently decided to take part in acting himself. That's why, from June to September and during other periods when he had no teaching commitments, he stayed in Brighton playing supporting roles in his wife's small drama company. During his extended absences, the only connection with him was the brief phone calls he made to us a couple of times a week, mainly to get updates on the cats he had left at his house in Cambridge. Each night, those most trusted among his researchers (I wasn't one of them) took turns caring for the cats.

I gained a lot from the time spent with Sam. First and foremost, from his corrosion course. A true actor - it's worth mentioning, he delivered his lectures impeccably, enriching them with numerous practical cases and stories from his professional life, always with great humor. I remember that every morning he entered the lecture hall habitually but late, exclaiming, "*Sorry, terrible the traffic this morning, boys*". Something quite unlikely in the tranquil Cambridge of those years. Then, from his research: upon my return, I brought several new measurement techniques learned in Cambridge to Milan, along with the decision to embark on the experimental study of the corrosive behavior of metallic materials within the human body, which he had been working on for several years. Finally, I gained lasting friendships formed in his laboratory during a year of close collaboration with colleagues from around the world.

And perhaps it's not over. Who knows if his way of spending his last years before retirement, alternating between teaching, research, and his hobbies without feeling guilty about it, might end up influencing me as well? (Don't worry, graduate students working on their theses, I don't have any cats).

Dany Sinigaglia and the Professor

Starting from the mid-1960s, Dany Sinigaglia, who was a highly skilled and tireless experimenter, tackled the study of localized corrosion with methodologies and techniques that were absolutely innovative for the time. He was one of the first to propose theoretical models for interpreting corrosion in occluded cells; to develop calculation methodologies to highlight the influence of electrochemical, geometric, and environmental factors in the onset and development of localized attack; to introduce fracture mechanics methodologies into the study of environmental failure.
I worked with Dany for 15 years, and during that time, I had the opportunity to appreciate his qualities as a researcher and teacher (he taught metallurgy), as well as his loyalty and uncompromising nature in not accepting compromises. Unfortunately, his premature death prevented him from fully demonstrating the extent of his character as he would certainly have become an important reference in the field of corrosion and metallurgy.

Dany was proud of the results of his research and, like all of us, he aspired to showcase and discuss them with Professor Piontelli, the charismatic head of the Institute. This used to happen almost every day.

As we have already mentioned, the Professor had a difficult personality and inspired all of us assistants with a reverential fear because he could be unpredictable in his reactions. One fine day, upon returning from one of the many conferences he attended, he fell ill with the flu and let it be known at the Institute. I conveyed this information to Dany, who was eagerly waiting to show him the results he had obtained in recent weeks. I understood that he was very disappointed about this turn of events. So, I came up with the idea for a prank. I waited a day and then told Dany that the Professor had called and asked for him because he wanted to know the latest research on occluded cells. “Since he couldn't find you, he asked me to tell you to come to his house. In fact, he said you must insist on being let in because his family wants to keep him isolated from the world while he's feeling fine and wants to know the latest results."

Dany, with a bundle of notes, graphs, and tables, rushed to the Professor's house, located in a city center building, and told the maid, who came to open the door, that the Professor absolutely wanted to see him. However, she did not let him in but called Mrs. Piontelli, who tried to send Dany away and make him understand that, given the Professor's condition, the visit was inappropriate. Nevertheless, faced with Dany's insistence, she went to talk to her husband, and he, surprised, declared that he was not interested at all in discussing the results obtained by his student at that moment. Thus, Dany was politely asked not to insist any further and to leave. In the end, he left, disappointed that he had not managed to breach the sanitary cordon imposed by the Professor's family.

As soon as he returned to the Institute, he told me everything. He was very upset and concerned. I must say that I also spent the week with a certain anxiety, thinking about what would happen upon the Professor's return.

The following Monday, as punctual as ever, the Professor showed up at the Institute and immediately appeared in the laboratory where I was working, which was adjacent to his office. He said to me, concerned, "I can't understand Sinigaglia. He came to my house and insisted to see me about his results on pitting. But what was the urgency? I was in bed with a fever." I interrupted and told him everything that had happened. As soon as he realized it was a joke, he burst into prolonged laughter. The tension that had built up disappeared in an instant.

DANY SINIGAGLIA

Venice - July 8, 1936
Milan - July 10, 1983

Dany Sinigaglia, on the left wearing dark glasses, with some colleagues attending a presentation at the Symposium on Offshore Corrosion & Protection in Paris in May 1979.

Bruno Mazza

Bruno Mazza was undoubtedly the person who had the most influence on the corrosion group that formed in the mid-1960s at the Politecnico di Milano, initially consisting of him, Sinigaglia, and the author. He wasn't just influential because of his work in this field, although it was important, but more for his work in electrochemistry. Nor was it just because he taught the corrosion course for a couple of years, although the influence of his lectures can be found in the first part of my book *Corrosion and Protection of Metallic Materials*. Above all Bruno was our moral compass for thirty years.

He graduated in 1961, receiving the gold medal as the best graduate of the year. In 1965, he was appointed to the prestigious position in electrochemistry, and in 1968, he was held in such high regard within our university that the Council of the Faculty of Engineering requested and obtained a chair for him from the Ministry of Education, even though he was just over 30 years old. However, in 1968, the student protests and the conflict with the Faculty changed the dynamics.

BRUNO MAZZA

Turin - October 27, 1936
Milan - August 2, 2004

His break with the Academic Authorities can only be understood if it is framed within the student protest that reached the Politecnico six months after the events of May 1968 in France. This break also related to the Authorities' attitude of refusing any dialogue with the students, while Bruno was drawn to the students' demands for change and their aspirations for a world without impositions, a more just and solidary world. They decided to cut short his career. They blocked the competition for the chair they had requested for him. They couldn't take away his teaching position, only because the Parliament granted automatic extensions and later the stabilization of positions. However, they stripped him of trust, respect, and even forbade him from publishing. They thought of marginalizing and humiliating him, but in reality, by pushing him to look beyond the academic world, they gave him new opportunities.

Mazza realized that a part of Electrochemistry had always been kept out of university classrooms. This part concerned the health and sometimes even the lives of those who worked in chlorine-soda plants with mercury cells; in the field of surface treatments of metals, especially those involving cyanide baths or chromate-based processes; in the pickling departments; in the lead or cadmium battery industry. At this point, and we are in the early 1970s, he made a revolutionary choice: he took his students to these places, documenting and denouncing the unacceptable working conditions and proposing alternative solutions that respected the dignity and health of workers. When I think of a civil hero, I think of Mazza during those years: he was undaunted by the warnings of the Academic Authorities, the threats of legal or police intervention, the flattery of the powerful, the dangers he exposed himself to, the pressures of worried friends. He continued resolutely on his path, following without hesitation what he considered his duty as a teacher and a man of science.

Today, those situations of dramatic harmfulness no longer exist. An era has thus ended. The credit goes to the civil and technological growth that has occurred over the past forty years, but it is especially due to those like him who put themselves on the line to make a change. Fortunately, time is a fair judge. Nearly two decades passed, and Mazza had the satisfaction of obtaining the chair that they had denied him twenty years earlier, of becoming the director of the Department from which they had tried to oust him, and of being called to occupy some of the highest positions in the University.

Dear Bruno, many of us remember you as a scientist, your seriousness, and your captivating teaching style, your civil commitment, your intellectual honesty, your selflessness, your courage, your consistency, your availability, your gentleness, your ability to treat every person with the same respect, your competence, your seriousness, and dedication in the many roles you held. We remember your masterful lectures, the course materials from which we learned electrochemistry, the hours you spent explaining things that were not clear to us. Above all, you were a fraternal friend with whom we shared a significant part of our journey in academia and in life. Some of us experienced your determination in defending principles you considered sacred and your inflexibility in not accepting situations or impositions you found unfair. No one ever saw you engage in recriminations or favoritism. No one ever saw you make or accept a recommendation. No one ever heard you appear bored or distracted when someone approached you. In recent years, I often criticized you because it seemed unfair to me that you were doing so much routine work for others - for students, secretaries, collaborators, staff, colleagues, the department, the doctoral program, the administration - taking away time and energy from what only you could do. I also did not accept that you were not using your position within the administration, your skills, your culture, and your prestige to procure resources and people to prevent the decline of the electrochemical tradition of our department. But in the end, you were right. You didn't put your students ahead of others, but you taught everyone. You didn't leave a school of electrochemistry or corrosion, but hundreds of engineers remember your teaching and draw inspiration from you in their work. You never did anything to put yourself at the forefront, and now, in your presence, everyone takes a step back.

Corrosion for Everyone

“Diseases of Metals” from the medical lexicon

The physical decay of metals is not solely within the domain of corrosion scientists. It is a universe that has also piqued the curiosity and interests of poets, writers, literary figures, and the Evangelist Matthew.

Those who have worked in the field of corrosion in the past have often drawn words, expressions and images from the world of medicine and, more generally, from human life to illustrate their problems. Of course, at times, the reverse has also occurred. For example, the term *caries*, which refers to the destructive process of a bone or, more commonly, a tooth, derives from the Latin “*caries”*, meaning corrosion. In Italian the adjective “*inossidabile*” (stainless in English*)*, originally coined to describe the family of steels that best resist aggressive environments, is now also used to refer to a person who maintains their health, validity, or prestige despite the passage of time or changing circumstances. And the term *restoration*, which originally indicated the operation of restoring a degraded work of art or prestigious object, such as a fresco, a building, a vase, or an ancient artifact, is now also applied to dental structures, faces with too many wrinkles, or breasts overly sensitive to the law of gravity.

The “patients” are not made of flesh and bone

But let’s go back to the initial discussion by recalling some words and expressions that corrosion experts have borrowed from the medical lexicon. Terms like pathology, diagnosis, prognosis, therapy, and prevention, which have identified various areas and phases of the medical field since the time of Hippocrates, have always been used in the field of corrosion as well. Of course, in this case, there are no flesh-and-blood patients, but rather objects, equipment, or predominantly metallic structures. In recent times, the term *equipment gerontology* has also come into use, mainly referring to the premature degradation of electronic equipment and the consequent need to extend their operational life.

Bronze cancer is a form of corrosion that terrifies museum curators who have artworks that have remained buried for centuries, covered by layers of corrosion products. When these artworks come into contact with the atmosphere, especially if it is humid and polluted, and if the innermost layer consists of cuprous chloride, they can be irreparably damaged. This chloride transforms into a bulky green product called “paratacamite,” which destroys the patina.

Tin pest is the transformation of white tin into gray tin, which occurs at very low temperatures. This process causes the metal to disintegrate, leading to the destruction of affected objects. An example is what happened during Napoleon’s disastrous campaign in Russia when the buttons on soldiers’ jackets and pewter dishes of his officers were affected by tin pest. Something similar occurred during Amundsen’s Antarctic expedition with canned meat sealed using tin soldering.

Sensitization of stainless steels is the process in which, at certain temperature ranges, chromium carbides precipitate at the grain boundaries. This can lead to intergranular attack in environments that are normally not aggressive to these steels, once they become sensitized, resulting in grain boundary cracking.

There is some similarity to specific allergic reactions in living organisms, where they develop abnormal responses when exposed to an allergen to which they have become sensitized.

Pitting is a form of localized attack on metals covered by protective films, leaving their surface pockmarked, much like smallpox affected a person’s skin. To describe its morphology, terms like ulcers, nodules, pustules are used. To specify the time delay between exposure to aggressive substances and its manifestation, the term “incubation time” is employed. To describe how it can be halted, the term “repassivation of the surface film” is used. To emphasize that prevention is much easier than treatment once it is initiated, it is said to be simpler to prevent than to cure.

Pietro Verri and the praise of prevention

A passage by Pietro Verri comes to mind from 1786, in the midst of the controversy between those who supported the introduction of mandatory smallpox vaccination to immunize entire populations against this scourge, and those who were against it. In *Il Caffè*, Verri praised prevention, saying, "this beneficial medicine that doesn't wait for the ailment to heal it but keeps vigilant and anticipates to prevent it." Truth be told, as we transitioned from the phase of phenomenological observations and the classification of degradation types, which we could call Linnaean, to a more rational framework, many medical terms fell out of use. Among these was the term "infection," used by Evans to describe the corrosion contagion that certain corrosion products could cause in the regions surrounding the affected area. Expressions like "*green rot*", which described the high-temperature attack that some nickel alloys undergo (although, as we've seen, this term has made a return in the field of corrosion), or "*green disease*", another name for bronze disease. In Italian "Butteratura" (*Pockmarking*) and "vaiolo" (*smallpox)* are variants of "pitting." "Candlot bacilli" describes the expansive salt, now known as ettringite, that forms in reinforced concrete structures when they are exposed to sulfate solutions. "*Byne disease*" referred to the clouding of calcareous shells in museums due to the acetic acid released by the wooden display cases.

At least until the 1950s and 1960s, the connection between corrosion and disease extended beyond specific terms or medical expressions used. Even prominent scientists in the field explicitly illustrated this connection. For example, Felice De Carli, in his book *La vita dei metalli* (The Life of Metals) from 1956, dedicated a chapter to "Pathology, Prophylaxis, and Metallurgical Therapies." He described the tin plague: "If kept at very low temperatures, white tin alongside a small amount of tin transformed into powder, one can observe that mere contact establishes a true contagion. White tin rapidly becomes covered in gray spots and, after a short time, it is completely sick, just as it happens in the human body due to the most dreadful diseases. Theoretically, tin should become susceptible to illness and sensitive to a deadly infection below 18°C. In practice, it becomes sick and deteriorates visibly only when the temperature drops below -30 to -50 °C.” In his introduction to the book *Elementi di teoria della corrosione a umido dei materiali metallici* (Elements of Wet Corrosion Theory of Metallic Materials) from 1962, Roberto Piontelli compared the field of corrosion to that of medicine and defined the figure of the corrosionist: “The field of corrosion can be closely compared to that of medicine. For metallic materials, corrosion is undoubtedly the most insidious cause of decay and death. The corrosionist is usually faced with the very challenging task of diagnosing the ailment, determining its causes, preventing it where possible, or otherwise suppressing it or keeping it within acceptable limits... To achieve this goal, one must build their atlas of pathological anatomy of materials exposed to various aggressive environments, establish the body of their diagnostics, and develop an increasingly effective anticorrosion pharmacology.”

When Carlo Emilio Gadda wrote about the “Duomo’s disease...”

In truth, not only men of science but also writers and poets have spoken of corrosion in terms of a disease. Some have done so to describe the physical phenomenon, while others have used it to illustrate the human condition. In the first category, for example, falls Carlo Emilio Gadda (Restauri del Duomo *Restorations of the Duomo* in La Lettura n. 1, 1-1-1936, pp. 61-65), who, as an engineer, albeit in his unmistakable style, describes the degradation caused in the statues of the Milan Cathedral by the corrosion of steel inserts. Since it is not often that we can cite a writer like Gadda to illustrate a case of corrosion and its consequences, let us quote almost in its entirety the passage in which he talks about this degradation.

“In the upper part of the Milan Cathedral, a harmonious command has assembled and deployed the cohort on the line of the spires: the Donatellian cohort of saints, white martyrs [...] and Filippino has designed the arches for all the dreams and prayers of the centuries. For the moment, the arches do not give cause for concern: but the saints are anchored to the pinnacle’s capital (which supports them like a plinth) by an iron pin. The weather, filtering into the support joint, has come to oxidize and swell the iron. In this way, the pin has acted as a wedge, causing the pedestal to crack and sometimes break cleanly: theoretically, the saint is free to fall, say with a stronger gust of wind than usual blowing from the right [...]. The same thing happens to the elements of the decoration. The striking pinnacle with pointed arches, terminating in an acute triangle with a bow, interspersed with spires (which in the jargon is called *falconatura*), is held together by a continuous key: this key, like a long stick onto which little birds with a delicate beak have been alternately threaded with strips of lard and sage leaves, swells over the years like any rusty iron forgotten on the rooftops: and it cracks the load-bearing parts of the ornament at statically vital points. This makes it necessary to replace the perforated elements: the corrosion of iron is the disease of the Cathedral."

At the time Gadda was writing, he probably did not know that the same disease had already appeared in London in St. Paul's Cathedral and had already been overcome, since 1925, by replacing ordinary steel with austenitic stainless steels (probably the first application of these materials in building restoration) and that it was causing significant damage in the temples of the Acropolis in Athens due to disastrous restoration work done at the beginning of the century using carbon steel inserts (and this time the problem was resolved later by using titanium inserts)

The corrosion is a pain, but it's also a big tit (La corosion xe malerbeta ma anche na gran teta)

Today, the Duomo's ailment has also been eradicated, and not only are the saints no longer theoretically free to fall, but neither is the Madonnina observing them from the highest spire. In fact, the iron dowels and long steel rods have been replaced with stainless steel AISI 316. The same has been done with other steel inserts used for reinforcement in statues or the building. Remarkably, in the case of the highest spire, the one with the Madonnina, the entire metal structure supporting it has also been replaced.

In the second category, we find poets and artists who speak of corrosion while thinking about human life and its fragility. For instance, in Shakespeare's *King Lear*, at the climax of the tragedy, the king's downfall is likened to the decay of nature and the world: "*O ruin'd piece of nature! This great world shall so wear out to nought!*" Oscar Wilde, in the solitude and desolation of Reading Gaol, sees the chain of life rusting: "*And thus we rust Life's chain, Degradated and alone.*" The evangelist Matthew, quoting the Sermon on the Mount, warns, "Do not store up for yourselves treasures on earth, where moth and rust destroy." The rock singer Neil Young, in one of his most significant albums, *Rust Never Sleeps* (1979), expresses the anxiety about life wearing away because, indeed, rust never sleeps, and he also conveys the dream of romantics throughout time to live life intensely, even if it means burning out rather than rusting: "*It is better to burn out than it is to rust*".

Corrosion experts are well aware of metals' tendency to return to the dust of their oxides and salts from which metallurgy had extracted them, and they experience every day how this return indeed occurs when the conditions of passivity, protective barriers, or electrochemical inhibitions gradually diminish under the impact of time. For this reason, they are the first to understand why so many poets, artists, or saints see in the life of metals and their return to their initial state a metaphor for their own lives and destinies.

Nevertheless, they do not view this phenomenon with fear. For many of them, corrosion is an opportunity to discover, think, and work, that is, to achieve scientific or professional fulfillment. For some, it is even a tool for fantasizing and playing, in other words, for living. And, in any case, for everyone, as implied by the rhyme from their English colleague (*Things rust, no doubts about it / but most of us would starve without it*) and the rhyme from our local jester (*La corosion xe malerbeta ma anche na gran teta*), it is a means to survive. In short, for those in the field, it's a remedy, not a disease!

Metal passivity: characteristics and diagrams

The fundamental discoveries made by the Belgian scientist Pourbaix have made it possible to determine the conditions that allow the formation of passive films.

Passivity is the condition in which metals are covered with protective layers of oxide or other compounds. Highly reactive materials themselves (such as stainless steels, aluminum and other corrosion-resistant metals like titanium, tantalum and zirconium) operate in this condition when used correctly. Moderately reactive and noble materials, on the other hand, do so only when they come into contact with certain environments. For example, carbon steels in concrete and copper alloys in seawater. Passivity is a very important and complex phenomenon.
The conditions under which it is established or lost are difficult to predict without a general framework.

Three very significant examples

To illustrate these aspects to the readers of his book, which primarily focuses on this topic (*Lectures on electrochemical corrosion*, Ed. Plenum Press, New York, 1973), Marcel Pourbaix presents the following three examples in the introductory chapter.
First example: in a laundry, the decision is made to soften the water to reduce soap consumption. This innovation leads to the corrosion of the water supply system, resulting in rust stains on the clothes that were supposed to be cleaned.
Second example: in a hospital, a similar decision is made. The water softening process causes the distribution system, partially made up of lead pipes, which had been functioning perfectly until then, to corrode rapidly. This leads to symptoms of patient poisoning.
Finally, the third example: before transporting a series of lead-acid batteries, a moving company decides to eliminate the danger posed by the sulfuric acid contained in the batteries by replacing it with distilled water. Within a few hours, the battery plates are destroyed.

After presenting these three examples, Pourbaix writes: "Their explanation will become clear as you read the text." We do not expect the same for the readers of this note. We will be satisfied if we manage to pique their curiosity and encourage them to delve deeper into the subject.

Historical overview

Towards the end of the 18th century, it was observed that under certain conditions, iron could displace silver from solutions of its salts, while under seemingly similar conditions, it did not react. This phenomenon was not thoroughly investigated until around 1840 when the study of the non-reactivity conditions of iron, already referred to as passivity at that time, was revisited by scientists like Faraday. The English scientist noted that iron, in concentrated nitric acid (fuming), remained unreactive, whereas in diluted nitric acid, it corroded vigorously and released nitric oxide gas bubbles.

Faraday also observed that in diluted nitric acid, iron did not corrode if it had been previously immersed in concentrated nitric acid, as long as its surface was not mechanically scratched. Furthermore, it did not corrode when connected to the positive pole of a battery and allowed to exchange current anodically with a cathode placed in the acid. Based on these observations, Faraday attributed passivity to the presence of an oxide layer on the iron surface.

In the subsequent decades, it was discovered that this phenomenon was not exclusive to iron but also applied to other metals like bismuth, tin and chromium. In fact, unlike iron, chromium could passivate simply by exposure to the air. Finally, in 1911, Monnartz highlighted that even iron-chromium alloys with chromium content exceeding 10.5%, namely stainless steels, exhibited similar behavior.

This last discovery transformed passivity from a scientific curiosity into a phenomenon with significant industrial implications, sparking the interest of researchers. However, it would take a few more decades for a true development of knowledge on this topic. There were three key milestones in this development.

The first milestone concerned the well-known potential-pH diagrams, commonly known as Pourbaix diagrams (named after the Belgian scientist mentioned earlier), who conceived, calculated, and later compiled them in the Atlas of Electrochemical Equilibria shortly after World War II. These diagrams allow, among other things, the determination of environmental conditions under which the separation of oxides or other compounds at the surface of metals is possible, leading to the formation of passive films, as well as conditions where such separation is to be excluded.

The second milestone relates to the so-called anodic and cathodic characteristic curves, which, as potential varies, define the kinetics of oxidation and reduction processes that can take place at the metal surface, thus determining its corrosion behavior.

The third milestone concerns the structural, compositional, and thickness characteristics of protective layers. In principle, knowledge of these characteristics should have preceded the others, but due to the extreme thinness of these layers, in many cases, it was acquired later.

Characteristics of protective layers

Protective layers can form on the surface of metals either through the precipitation of corrosion products from solutions where their concentration has reached saturation limits, or they can be produced directly on the metal surface as a result of its anodic functioning. The first mechanism gives rise to relatively thick and often porous layers, generally non-conductive. Examples include lead in sulfuric acid, silver in chloride solutions, and copper or bronze exposed to the atmosphere. Surface treatments such as steel phosphating and bronze patination also result in such layers.

More importantly, the second mechanism primarily affects transition metals or their alloys (iron, chromium, molybdenum, tungsten, titanium, zirconium and their alloys, including stainless steels), and some non-transition metals like aluminum. Up until the 1970s, two schools of thought debated this second type of passivation: one attributed it to the formation of a monomolecular layer of adsorbed oxygen, while the other believed it to be produced by a true oxide film capable of isolating the metal from the aggressive environment.

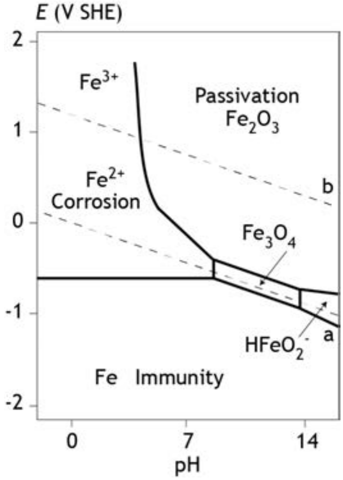
Surface analysis techniques such as ellipsometry, which has the ability to detect the presence of monoatomic layers, and Auger spectroscopy, which can determine composition profiles within layers a few nanometers thick, have clarified this issue. In only a few cases and conditions, monoatomic layers of adsorbed oxygen are formed, which tend to transform into thicker layers over time. In general, true transparent films are formed, with typical thicknesses ranging from 1 to 10 nm and often exhibiting semiconductor-like properties.

Significantly thicker oxide layers can also be produced artificially. For example, the anodic oxidation of aluminum allows the creation of oxide films up to 10 μm in thickness, while those formed through natural exposure to the air or other environments generally do not exceed 10 nanometers. In this case, thicker films provide greater protection compared to thin films.

However, this is not always the case. In the case of stainless steels, oxide films observed in heat-affected zones from welding processes, with thicknesses in the hundreds of nanometers, producing interference colors, or even the thicker black scale seen on their surfaces when they come out of mills or drawing facilities, are not protective at all. In fact, they must be carefully removed through appropriate pickling so that a protective film, starting from the bare metal and preferably in the right environment, can form, typically a few nanometers thick.

Different situations

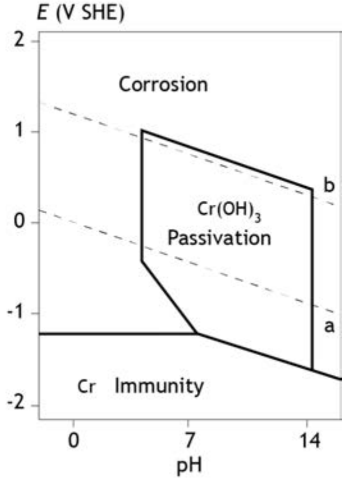
The passivating layers that form on the surface of pure metals consist of various oxides (for example, on iron, you can have $Fe(OH)_2$, Fe_2O_3, Fe_3O_4) or compounds of the metal itself. Their adhesion to the metal surface, and thus the degree of protection hey provide, depends on their nature and structure, as well as the composition of the environment in contact with the metal. For instance, chlorides have a peptizing effect on deposits, causing them to disperse in the environment.



Simplified Pourbaix diagram of iron: At the bottom, we find the region where the metal does not corrode because it has no tendency to do so (immunity zone). On the left and far right, there are regions where it dissolves in solution as Fe^{2+} and Fe^{3+}, and as $HFeO_2^-$ (corrosion zones). On the right, there are regions where it tends to form magnetite (Fe_3O_4) or hematite (Fe_2O_3) layers. The diagram also includes lines indicating the equilibrium potentials for the cathodic processes of oxygen reduction and hydrogen evolution.

Additionally, the adhesion and protection provided also depend on the coexistence of other types of deposits on the surface. For example, the formation of carbonates on the surface of steel in contact with potentially scaling waters promotes the adhesion of the iron oxides that form on the surface, enhancing their protective action. It's important to note that if these iron oxides do not form, the calcium carbonate deposit does not provide sufficient protection.

In the case of alloys, the situation is more complex because various metal oxides can be formed. However, often only one component is capable of passivation, while the others dissolve into the solution. As a result, the surface layer of the material is dominated by, or even exclusively composed of, the most resistant constituent. For example, Auger surface analyses reveal a strong enrichment of chromium on the surface of stainless steels, allowing the formation of a protective film primarily composed of chromium oxide (Cr_2O_3). It is due to this enrichment that stainless steels, even though they are primarily composed of iron and often contain significant levels of nickel, exhibit corrosion behavior similar to chromium. Consequently, they resist corrosion in many acidic environments where iron and nickel are prone to corrosion.

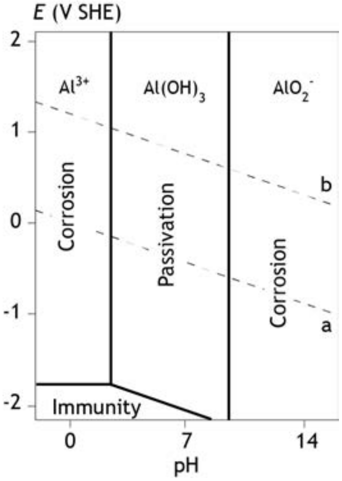


Simplified Pourbaix diagram of chromium: please note its greater ease of passivation compared to iron, but also one of the weaknesses of this metal (and therefore of stainless steels) that can corrode in reducing environments (low potentials) even in solutions close to neutrality and at very high potentials.

Potential/pH diagrams

In 1945, Pourbaix, at Delft, successfully defended his thesis on the *Thermodynamics of Dilute Solutions*. This marked the birth of the potential/pH diagrams, more commonly referred to as Pourbaix diagrams. Pourbaix's work presented the role of pH and potential in these diagrams. In Pourbaix diagrams, you typically find information for each metal regarding the pH and potential ranges in which the metal corrodes, the ranges where it is corrosion-immune, and those in which the formation of surface films, which may or may not be protective, is possible. The diagrams also include the equilibrium potentials for cathodic processes of oxygen reduction and hydrogen evolution, which define the maximum potential values to which the metal is exposed in oxidizing or reducing environments.

To avoid misunderstandings, it is necessary to clarify the difference between the term "passivation," which is found in Pourbaix diagrams to indicate the regions where the separation of oxide layers is possible, and the term "passivity" that we have used so far. Passivation refers to the processes leading to the formation of layersThese processes result in passivity conditions and, consequently, in the actual protection of the metal, but only if they occur over the entire surface and produce adherent layers without gaps or defects. However, if the layers produced do not



Simplified Pourbaix diagram related to aluminum: it is certainly worth noting in this case the amphoteric behavior of this metal, which can only passivate in the pH range around neutrality but not in acidic or alkaline environments, both in the absence and presence of oxygen.

possess these characteristics, as can happen, for example, in the case of stainless steels or iron in the presence of chlorides, they are not protective. In conclusion, the areas indicated in the diagrams as passivation zones are not always areas where passivity conditions are established, even though they are the only areas where this can occur.

Pourbaix diagrams hold a position in the field of corrosion similar to what phase diagrams, such as the Fe-C diagram, have in metallurgy. Just as these phase diagrams serve as the foundation for understanding the structure of alloys, even though the actual structure may consist of metastable phases, Pourbaix diagrams provide the conditions for the formation or disappearance of oxides or compounds as predicted by thermodynamics. However, in practice, due to structural or surface phenomena, these conditions are not always met.

Current/potential curves

The anodic and cathodic characteristic curves, also known as anodic and cathodic polarization curves, or Evans' curves, describe how the kinetics of oxidation and reduction processes change with varying potential on materials. These curves allow for a precise determination of the actual corrosion behavior of materials. To continue the previous metallurgical analogy, in the field of corrosion, they play a role similar to what TTT (temperature, time, transformation) curves, also known as Bain curves, have in metallurgy.

The importance of these curves and how to use them has been known since before the war when Evans proposed them. Experimental determination of these curves for passive materials became practically feasible only in the 1950s when a specialized instrument, the potentiostat, entered electrochemical laboratories, thanks to advances in electronics.

The availability of these curves had immediate consequences. The ability to quickly and accurately evaluate the corrosion behavior of materials led to improvements in the composition of established materials like stainless steels, which had been in use for almost half a century at the time. It also enabled a correct prediction of the suitability of materials based on titanium, niobium, zirconium, tantalum, which had just appeared on the industrial application scene in aggressive environments.

Moreover, new metallic materials with corrosion-resistant properties previously considered impossible were developed, such as the titanium/palladium alloy, which has the rare and valuable characteristic of resisting both oxidizing and reducing environments. New techniques like anodic protection were applied, allowing materials like carbon steel, stainless steel, and titanium to be artificially kept in a passive state in highly aggressive environments. Finally, an understanding emerged of how and when different factors (electrochemical, environmental, mechanical, and metallurgical) can compromise passivity conditions and trigger localized attacks, which are the weak points of passive materials. In short, many new developments occurred.

Will it corrode? Two different ways to pose the question

Indeed, the first way is simple, straightforward, and direct, while the second is certainly less immediate but places a focus on understanding the corrosion mechanism

The first question that a corrosion scientist asks when evaluating the behavior of a metallic material in a corrosive environment is this: “May the material corrode?” If the corrosion scientist is also a professor, they pose the same question, but in a less direct manner: “Is there a driving force available for the metal to transition from the metallic state to that of combination with substances present in the aggressive environment?” Unfortunately, the answer is almost always “yes.” There is an exception for gold, which is more stable than its corrosion products, fortunately allowing us to find nuggets. Other materials, less noble than gold, like silver, copper, or their alloys, can also be exceptions, but only in environments where oxygen or other oxidants are absent. Even less noble materials like iron or nickel can be exceptions, but only when they are cathodically protected.

As you can see, these are significant but isolated cases. In general, materials tend to corrode. Even those considered the most resistant, such as stainless steels, superalloys, titanium, niobium, and tantalum, exhibit this tendency. The reason they don’t corrode rapidly is because they are covered by protective films made up of their own corrosion products.

Knowledge of the phenomena

The answer to the first question, which the professor might call thermodynamics, does not help much except in very few cases when it is negative. It is not possible to reject materials solely because they can corrode, especially when they corrode very slowly, taking, for example, centuries or even millennia for the attack to penetrate fractions of a millimeter.

Therefore, our corrosion scientist must ask a second question, which could be termed kinetic, and that is: “If the material can corrode, at what rate does it corrode?” Until the 1960s, the answer to this second question was generally qualitative, primarily based on knowledge derived from previous experiences or empirical tests. Today, it is quantitative and based on an understanding of the corrosive phenomena and the laws that govern them, which are electrochemical laws. Much information is derived from simple operational tools, such as anodic and cathodic polarization curves, which allow the assessment of material behavior and provide insights into the oxidizing power of the environment, thus enabling the determination of corrosion rates and the influence of environmental or material-related factors.

In this context, after explaining the mechanism of the corrosive phenomenon, we will describe these curves and the so-called Evans diagrams, named after the English scientist who, through his studies starting from the 1920s, made all of this possible, along with their applications.

The electrochemical mechanism

Corrosion processes occur through an electrochemical mechanism because the overall corrosion reaction consists of two electrochemical reactions. The first, called the anodic reaction, transforms metal atoms into ions while simultaneously releasing electrons within the metal. This is the part of the corrosive process that we observe, such as iron rusting, or copper, zinc, chromium, or nickel ions going into solution or being covered by their corrosion products.

The second reaction, called the cathodic reaction, consumes these electrons to reduce species present in the environment. In aerated environments, i.e., those in contact with the atmosphere, the most common cathodic reaction is certainly the reduction of oxygen. In acidic solutions, or in the absence of oxygen or other oxidizing species, the most frequent reaction is the evolution of hydrogen. Under specific conditions, other reduction reactions involving different oxidizing species in the environment, such as ferric, cupric, chromate, nitric, or chlorine ions, can also occur.

Since the corrosive process does not alter the electrical state of the system, the number of electrons made available by the anodic process at any given moment must equal the number of electrons consumed by the cathodic process at the same time. This implies that (1) a current (i_a) flows anodically at the metal surface (i.e., a current passing from the metal to the solution), and a current (i_c) flows cathodically (i.e., a current passing from the solution to the metal), and (2) these two currents, i_a and i_c, must be equal, $i_a = i_c$.

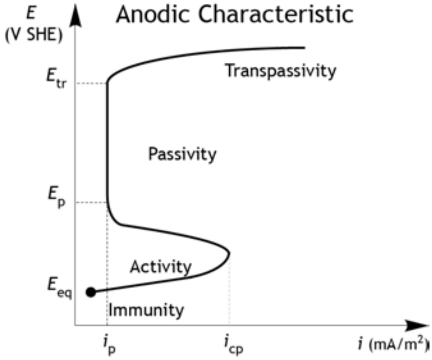
Consequently, the oxidation rate of the different elements constituting the metal and the reduction rate of the various cathodic reactants, as measured by i_a and i_c, must also be equal to each other. This common value is referred to as the corrosion rate or "current density" (i_{corr}): $i_a = i_c = i_{corr}$. Since the rates at which these two processes occur depend on the potential, the material reaches a potential (known as the free corrosion potential, E_{corr}) at which the equality just described is met.

Polarization curves

The curves that show how the rate of the anodic or cathodic process changes with varying potential are called polarization curves or potential/current density characteristic curves (E/i), either anodic or cathodic. These curves play a crucial role. The anodic curve provides insight into the corrosion behavior of the material in the considered environment; it's a kind of identity card for the material concerning its corrosion behavior. The cathodic curve measures the oxidizing capacity of the environment. When these two curves are combined, they allow us to determine the operating conditions of a material in the given environment, particularly the corrosion rate and the potential it operates at. In this note, we refer specifically to s*tainless steels, but the concepts discussed can be extended to all metals.*

Anodic curve. In the case of stainless steels and, in general, metals that can form protective films, the anodic curve follows the pattern shown in the figure.

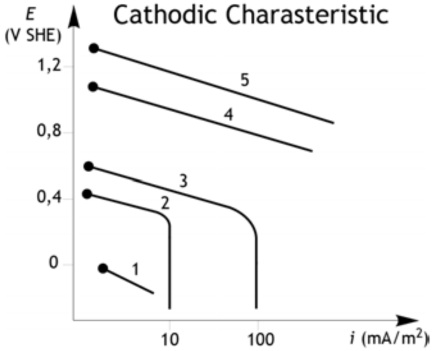
The passage of metal into the solution can only occur above a potential known as the equilibrium potential (E_{eq}). Below this potential, the steel is in a state of immunity, meaning it does not tend to dissolve but rather to deposit.



Typical Behavior of the Anodic Polarization Curve (Anodic Characteristic) of Stainless Steel.

As the potential increases above E_{eq}, in an initial range of potentials (referred to as the activity range), the metal dissolves with an increasing rate (measured by the current density, i). When the potential corresponds to the formation of surface films (passivation phenomena), the exchanged current drastically decreases to nearly negligible values (passivity conditions). The current remains at these values in the subsequent range of potentials (passivity range) and then starts to increase again at very high potentials (referred to as transpassivity range), which leads to the destruction of the film.

Cathodic curves. In the figure, characteristic curves for the reduction of oxygen (two curves for two different oxygen concentrations in the environment), hydrogen evolution, and typical curves for processes with very high oxidizing power (e.g., reduction of ferric ions, chromates, nitrates, etc.) are shown. Of course, the position of these curves depends on the concentration of various species participating in the reaction in the solution and often on the agitation conditions of the solution itself.



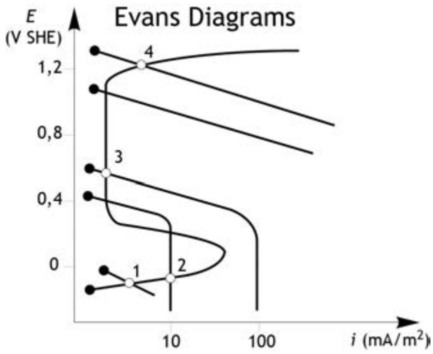
Qualitative behavior of cathodic polarization curves (cathodic characteristics) of some processes: 1 - hydrogen evolution; 2-3 oxygen reduction; 4-5 processes with high oxidizing power.

The Evans Diagrams. Let's now superimpose the characteristic anodic and cathodic curves to determine the operating conditions of the corrosive system stainless steel/environment. In the absence of oxygen or other oxidizing species, with hydrogen evolution being the only possible cathodic process, the operating conditions are represented by point 1 in the activity zone.

With the addition of oxygen or other oxidizing species, the corrosion rate initially increases (point 2), and then, from the moment when the cathodic characteristic no longer intersects the active branch of the anodic one, it drops to very low values typical of a material covered by the passive film (point 3). Finally, and only in the presence of particularly strong oxidizing species that raise the corrosion potential to very high values (point 4), the corrosion rate starts to increase again, and the material operates in transpassivity conditions.

The parameters that define their stainlessness

To fully characterize the corrosion behavior of stainless steel, which includes specifying its tendency to form a protective film and the degree of protection provided by this film, it is essential to have knowledge of the entire anodic polarization curve. This curve provides a range of parameters that can be derived from its characteristic points, as indicated in our initial figure.



Evans diagrams for stainless steel in environments with different cathodic processes.

The parameters in question are:

- Passivation Potential (E_p) and Transpassivation Potential (E_{tr}): these define the extremes of the potential range within which the material is in a state of negligible attack.
- Passivation Current Density (i_p): this measures the rate of such attack.
- Critical Passivation Current Density (i_{cp}): this defines the minimum current density that must be exceeded, at the primary passivation potential, to transition the material from an active state to a passive state.

It is evident that the corrosion behavior improves when i_p decreases, and when the range (E_{tr} - E_p) of passivity widens. It also improves when i_{cp} decreases, facilitating the transition of the steel from the active to the passive state.

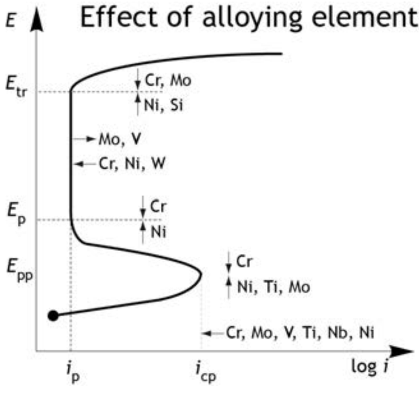
The parameters that define the corrosion behavior of stainless steels, particularly E_p, E_{tr}, i_{cp}, and i_p, depend on both environmental conditions and alloying elements.

Influence of Environmental Conditions. Increases in temperature, acidity, the concentration of aggressive ions, especially chlorides, tend to decrease the width of the passivity range and increase i_p and i_{cp}. In extreme cases, the anodic curve can lose its typical S-shape.

Influence of Alloying Elements. Regarding the influence of alloying elements, an improvement in the parameters defining corrosion behavior is observed when transitioning from martensitic stainless steels to ferritic stainless steels and, even more so, to austenitic stainless steels. This improvement is also seen when increasing the chromium content within austenitic stainless steels or moving from those without molybdenum to those with molybdenum or towards superalloys.

Chromium is the essential and irreplaceable element in the formation of the passive film, although other elements can contribute to enhancing its characteristics. With a chromium content of just 10.5%, the protective film forms, but it only resists in mildly aggressive environments, such as unpolluted atmospheres. With a chromium content of 17-18%, as found in the most commonly used austenitic types, resistance increases significantly. The resistance reaches very high values when the chromium content rises to 30%, as in the case of super-ferritic or super-austenitic stainless steels.

Nickel stabilizes the austenitic structure and enhances mechanical properties and workability. It doesn't significantly change the passivity conditions (i.e., i_p) but reduces the primary passivation current (i_{cp}), thus promoting the transition from active to passive conditions in acidic and reducing environments. Molybdenum and nitrogen, in combination with chromium, are highly effective in increasing the protective properties of the film, especially in the presence of chlorides. The following illustration provides a general indication of the influence of various alloying elements on these parameters.



Graphical representation illustrating the effect of certain possible alloying elements in stainless steel (e.g., chromium, nickel, molybdenum, nitrogen, tungsten, copper, vanadium) on the anodic polarization curve.

Composition of Materials, Corrosion Factor

In the arena of corrosion processes, two main actors always play a role: the nature of the metal and the quality of the environment in which it is located. Let's examine the first actor.

On the stage of corrosive processes, there are two main actors: the metallic material and the environment. This intervention focuses on the first of these two protagonists and aims to highlight how corrosion behavior depends on the composition of the metal, meaning its nature, the ratio of its constituents, the quality, and the content of impurities within it. The material also influences corrosive processes through its structure, which includes the type of crystalline lattice of its phases, the type and density of defects present, the morphology and size of grains, and the microstructural characteristics of their boundaries. It also involves the nature, density, distribution, position, shape, and extent of any inclusions, the surface condition, and so on.

It's not always possible to separate the corrosion effects related to composition from those originating from the structure, as one can influence the other. In this context, we limit our discussion to considerations regarding the composition.

Sometimes, more reactive materials are more resistant

It is well known that iron behaves differently in terms of corrosion compared to chromium or nickel, titanium compared to tantalum or aluminum, gold compared to copper or silver, zinc compared to lead or tin, low-alloy steels compared to stainless steels, and so on. By changing the nature or composition of the material, its thermodynamic nobility changes, which means its tendency to combine with oxygen or other substances present in the environment changes. But, more importantly, what is known as the kinetics of the corrosion process changes. This means that the opposing forces to the progression of anodic and cathodic reactions change, and the protective characteristics of oxide films or other corrosion products that form on its surface also change.

Generally, it is the kinetic effects that prevail. As a result, more reactive materials, which are those that more easily form oxide layers, often turn out to be the most resistant materials. This is evident even in the group of metals just mentioned. If we exclude gold, which is immune to corrosion in most environments, the materials that offer the best resistance are titanium, tantalum, chromium, and stainless steels. These are metals and alloys that thermodynamics place at the lower end of the nobility scale.

Formation of protective films

The most common obstacle that often prevents or completely stops the corrosion process is the formation of surface films. All metals belonging to the realm of stainless materials exhibit excellent corrosion resistance precisely because their nature and composition allow for the formation of these protective films.

In the case of alloys, it is often one of the constituent elements that imparts this characteristic. For example, chromium, when present in concentrations exceeding 12%, makes stainless steels resistant to corrosion in many environmental conditions because it ensures that their entire surface is covered by a chromium oxide film.

However, secondary elements, even when present in small concentrations, often become part of the composition of the surface film, which is primarily composed of the oxide of another metal, and enhance its characteristics. This is the case with iron in cupronickel, tin or aluminum in brass, molybdenum or nitrogen in stainless steels. Their presence not only changes the material's resistance to general corrosion but also its resistance to forms of attack that cause perforations or cracks, such as pitting corrosion, erosion corrosion, and stress corrosion.

Elements that lead to phase separation at grain boundaries or within the metal matrix weaken protective films. Therefore, their content should not exceed very low critical values. For example, carbon in austenitic stainless steels should not exceed 0.03% to prevent sensitization during welding, where the grain boundaries lose their passivation capacity. Another example is sulfur in carbon steels used in sour environments in the petrochemical industry, which should be kept below 20 ppm to prevent hydrogen-induced cracking.

In rare cases, passivity conditions are achieved through the presence of elements that do not oxidize and do not become part of the protective film's composition. For example, when palladium is present in titanium at concentrations between 0.1-0.2%, it imparts the rare and highly appreciated characteristic of withstanding both oxidizing and reducing environments.

The role of palladium is not to enhance the protective characteristics of the titanium oxide film, which are already exceptionally high, but rather to enable its formation even in less oxidizing environments. Paradoxically, this is achieved by stimulating the corrosion of titanium.

A similar situation occurs, in specific environments, with stainless steels when coupled or alloyed, even if only superficially, with platinum. For those who wondered what purpose platinum served in stainless steel, especially when shaving with blades called "platinum plus" produced by a well-known brand a few years ago, the answer might lie here.

There are impurities and impurities

Increases or decreases in the dissipation that occur in electrolytic processes and their respective accelerating or inhibiting actions on the corrosion rate are primarily observed when the cathodic process involves the evolution of hydrogen. The corrosion of less noble metals, such as aluminum, zinc, or cadmium, in acidic environments occurs through a similar mechanism. These metals, like all base metals, are characterized by a high overvoltage of hydrogen, meaning they do not catalyze its evolution. This is why their corrosion takes place at a negligible rate, despite having a high driving force for corrosion due to their low nobility.

Things change when the impurities are high-noble metals and therefore have a low overvoltage of hydrogen. The presence of such elements, in concentrations of around 0.1-0.2%, is sufficient to produce increases in the corrosion rate by several orders of magnitude. This happens when transitioning from pure zinc or aluminum to commercial zinc and aluminum, primarily due to the iron impurities that are always present in the latter materials. The negative influence on corrosion resistance due to the presence of tiny amounts of impurities had led to the belief, until the mid-1920's, that a perfectly pure metal without structural imperfections, if it were possible to produce, would be completely corrosion-resistant.

In fact, if the cathodic process is not the evolution of hydrogen but, for example, the reduction of oxygen, as is often the case in natural environments or aerated solutions, the influence is not always negative. Typically, even in this scenario, purer metals exhibit better performance than less pure ones.

As early as two hundred years ago, Fabbroni explained this behavior with two specific observations: "*I have preserved pure tin for many years without observing any change in its bright appearance, which makes it look similar to silver, while various alloys of this metal prepared by me for various uses have shown different behavior. And I have also seen Etruscan inscriptions on plates of pure lead perfectly preserved in the museum of Cortona. Instead, in Florence, in the gallery known as "I Piombi", the medals of various popes, made of lead with small additions of tin and perhaps arsenic to make them more beautiful and durable, have completely decomposed into a white powder or converted into oxide, even though they were wrapped in paper and stored inside a display case.*"

However, if the cathodic process involves the reduction of oxygen, there are cases where impurities lower the corrosion rate. This occurs primarily when they contribute to the formation of protective films. For example, zinc anodes for the cathodic protection of marine structures become passive if they contain iron in concentrations exceeding 14 parts per million (50 parts in cases where cadmium and aluminum are also present in the metal matrix). Similarly, steel structures containing small amounts of copper, chromium, or phosphorus and exposed to lightly polluted atmospheres develop protective patinas. As long as sulfur is absent, as it tends to be harmful.

Enrichment, impoverishment, and selective attacks

At the metal surface, there are enrichments or impoverishments of the various constituents compared to their concentrations in the bulk of the material. Let's consider an example of brass consisting of copper (70%) and zinc (30%). The two metals are completely soluble in each other. When in contact with an aggressive solution, the composition at the surface of the alloy tends to change because zinc and copper have different tendencies to go into solution.

In some cases, these chemical changes not only affect the surface but also penetrate deeper, resulting in what is called selective attack. This phenomenon occurs with brass alloys that can lose zinc (known as dezincification) while the copper remains in a porous form, or with cast irons, which can dissolve iron (a process known as graphitization).

Dezincified or graphitized artifacts maintain their shape but lose their mechanical and functional characteristics. With the materials used today, these two processes do not occur on a large scale. However, they can still manifest on the surface, causing a change in the electrochemical behavior of brass and cast iron, making it similar to that of copper or carbon. This can lead to galvanic corrosion when in contact with other materials.

While these two examples are significant, there are also other cases of selective attack, such as dealloying of aluminum bronzes, tin dissolution in phosphor bronzes, attack in other copper alloys involving manganese, nickel, cobalt, and so on, or in copper-silver, gold-silver, or lead-tin alloys, which respectively involve copper, silver, and tin.

Sir Winston, arsenic, … and antique lace

The importance of chemical composition, even concerning elements present in small quantities, can be illustrated by the changes that occurred in the early 1920s in the tubes of seawater-cooled capacitors. Today, the problem of their corrosion is resolved by using traditional copper alloys and other materials, including titanium. However, back then, it was a different story.

In 1919, during a parliamentary speech, Winston Churchill, who was then an Undersecretary of the Navy, stated that during the recently ended war, the damage and malfunctions caused to the British fleet by the corrosion of capacitor tubes far exceeded the damage inflicted by the German Navy. The economic, military, and strategic significance of the issue necessitated special research efforts.

Understanding the corrosive processes that were disabling the capacitors led to the development of new materials like aluminum brass, cupronickel, and an improvement in capacitor design to control turbulence conditions and reduce the possibility of deposit formation. As a result, during World War II, the unavailability of ships due to capacitor corrosion was significantly reduced compared to the previous conflict.

The breakthrough in solving the problem occurred in 1924 when two researchers, Bengough and May, found a way to prevent the most insidious of the three forms of corrosion affecting brass alloys: dezincification.

Returning to the capacitor tubes in use during World War I, they were either made of single-phase brass with 70% copper and 30 % zinc or Muntz metal, a two-phase alloy composed of 60% copper and 40% zinc. These materials were subject to essentially three types of attacks: selective zinc attack, namely dezincification, attack under deposits, and corrosion caused by seawater turbulence.

The solution for the latter two types of corrosion could be glimpsed, as the causes behind them were evident. However, that was not the case for the first type of attack. In fact, the behavior of the tubes regarding dezincification was a real mystery.

Under apparently identical conditions, some tubes developed a green protective patina of atacamite, a basic copper chloride, while in other cases, a white or brown film of basic zinc chloride grew. Under the green patina, the brass remained intact, while under the white or brown film, there was selective dissolution of zinc, transforming the brass into a spongy layer of copper. This process could continue until it affected the entire tube wall, leading to the destruction of its mechanical and functional properties.

The mystery was unveiled in 1924 by the aforementioned two researchers who noticed that protective patinas formed on tubes made from brass containing arsenic in concentrations greater than 0.01%, while non-protective patinas formed on tubes made from materials lacking arsenic. In other words, as in a respectable mystery, everything revolved around arsenic: why the different behavior of brass towards selective zinc attack was due to its presence or absence.

At this point, the remedy became obvious: the addition of small percentages of this element. Shortly after, it was found that antimony and phosphorus produced similar effects in similarly modest quantities.

This led to the discovery of the beneficial effects of adding tin (1%) and aluminum (2%). This gave rise to *Admiralty* brasses, *naval* brass, aluminum brass, and eventually cupronickel tubes.

Tubes made of titanium or stainless steel would come much later.

Corrosion phenomena due to galvanic contact

A comprehensive analysis conducted on the issues related to the electrochemical attack that can lead to material degradation.

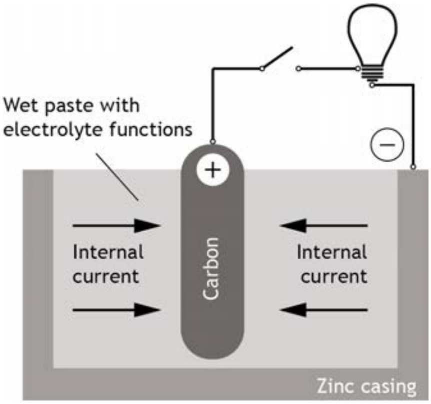
Galvanic contact corrosion occurs when two metallic materials of different nobility come into contact in the presence of an electrolyte. The metal with the more negative potential - the anode - corrodes, while the one with a more positive potential - the cathode - remains protected. Not only metals can function as cathodes, but also other materials with electronic conductivity. Among these, some particularly important ones are magnetite, which forms on steels near welds or during hot working (calamine or black scale from rolling), or graphite, which may come into contact with metals for various reasons, such as its use as a lubricant or for other purposes. In specific cases, other oxides, sulfides, or various compounds may become important.

In the vast majority of cases, the cathodic surface undergoes the process of oxygen reduction. However, in specific environments and conditions, other processes can occur, such as the reduction of hydrogen ions to form hydrogen or the reduction of oxides, ionic species, or neutral compounds.

It operates like a battery

The system that leads to galvanic corrosion functions similarly to one of the batteries we use every day. The current, inside the electrolyte, which consists of the aggressive environment, flows from the metal that corrodes - the more negative or less noble of the two - to the one that is protected - the more positive or nobler - and in the opposite direction in the external metal circuit.

Just like in the case of a battery, the driving force that propels the current is provided by the potential difference that can be measured - in an open circuit - between the two metals (or the two electrodes). However, there is a difference here. While the battery provides external work (it lights up the bulb) the system that leads to galvanic



Galvanic contact corrosion operates similarly to that of a battery; in the diagram - a typical 1.5 V Leclanché cell - the carbon, which serves as the positive electrode and acts as the cathode, functions like the noble metal in the galvanic coupling. The zinc, serving as the negative electrode and acting as the anode, is the less noble metal that corrodes. The moist paste in between serves as the electrolyte.

corrosion is short-circuited and, therefore, dissipates everything within itself.

A bit of history

Galvanic corrosion, or rather its effects, must have been observed in antiquity, as evidenced by the discovery of bronze nails used to fasten lead plates with their heads covered in lead in certain wrecks of Roman ships. This practice was carried out to prevent the harmful effects of galvanic coupling. There is no other explanation, considering that bronze is more resistant than lead.

At the end of the 18th century and in the following decades, this form of corrosion played a significant role in the development of electrochemical science. It was the observation of its effects that allowed a distinguished Tuscan scientist, Giovanni Fabbroni, "*to establish the chemical theory of galvanism and lay the foundations for the galvanic theory of corrosion ten years before Volta's invention.*" (These words are from Professor Roberto Piontelli, who was an authority on the subject).

Thirty years later, in 1824, studies on the effects of zinc-copper and cast iron-copper couplings led Davy to recommend to the British Navy the use of zinc or cast iron anodes to protect the copper sheets covering the submerged part of wooden ships of the time. Naturally, Davy was more interested in the protection provided by zinc or cast iron on copper than in the corrosion that the coupling induced on cast iron and zinc; his was a desired case of galvanic corrosion. But the phenomenon is the same.

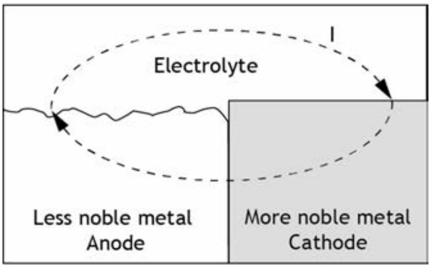
Beneficial effects

Galvanic corrosion can also be beneficial, although in such cases, we don’t refer to it as corrosion but rather as a cell or cathodic protection. Speaking of desired cases of galvanic corrosion, another curious and more domestic example is used to clean silverware, which tends to tarnish. Place the silverware in an aluminum pot filled with water. Add baking soda and, to speed up the process, bring it to a boil. After some time, the stains disappear (or mostly). Perhaps with the help of a rinse. In fact, the stains are caused by silver sulfide. The current produced by the contact between silver and aluminum causes the reduction of silver sulfide and a slight surface corrosion of the aluminum. It doesn’t remove the silver - or rather silver sulfide - as when cleaning is done manually. Of course, instead of an aluminum pot, which is now hard to find in the kitchen, you can use a basin made of the same metal or place a sheet of aluminum on the bottom of an enameled or glass container. The more refined and well-equipped individuals, to enhance the galvanic effects, replace aluminum with magnesium. But it’s always a case of galvanic corrosion.

The four principal factors

The purpose of this note is to explain the four principal factors that govern galvanic corrosion and, at the same time, highlight the role that stainless materials, especially stainless steel (or inox), play concerning this type of corrosion in all their possible applications. This is not so much because they undergo the attack, but because they can induce it in the materials to which they are connected.

These four factors are: the difference in practical nobility between the coupled metal; the catalytic properties of the nobler metal regarding the cathodic reaction, the electrical conductivity of the electrolyte, and the ratio between the areas of the two coupled metals effectively functioning as anode and cathode. In the first part of this note, we will only consider the first of these factors.



Galvanic Corrosion Diagram: Attack occurs on the less noble material while the nobler one remains protected, only when the surface is in the presence of an electrolyte. Naturally, in the cell formed this way, the current flows from the anode to the cathode in the electrolyte and from the cathode to the anode in the metal circuit. In fact, in the solution, current is carried by ions, and in the metal, it's carried by electrons.

There's nobility and then there's nobility

The coupling of two materials leads to galvanic corrosion only if they have different *nobilities.*

Knowledge of the values that this parameter takes for various materials in different operating conditions - in other words, knowledge of the nobility scale of metals - is crucial to understand which materials can or cannot be coupled in various conditions. This also helps determine which material in the coupling corrodes and which remains protected.

The *thermodynamic nobility* of a metal is defined as the equilibrium potential it assumes when placed in a solution. The scale of thermodynamic nobilities is given by the electrochemical series of potentials, which is considered standard when all species involved in the process have unit concentration. Metals with high potential, placing them high on the scale, are considered noble.

While this scale can provide some guidance, it is insufficient to assess whether or not corrosive attacks will occur when two metals are coupled. To make this determination, you must know the potentials that metals assume in the specific environment under the actual conditions they encounter, which are typically not in equilibrium. This requires knowledge of the *practical nobility* of different metals, measured by their actual potentials. These practical nobilities can vary significantly from the equilibrium values, especially when metals corrode or are covered with oxides.

Unfortunately, *practical nobility*, along with the corresponding potential, depends on composition, temperature, the presence of oxygen or other oxidizing agents, agitation, and especially the presence of oxide films or other compounds on the material's surface. Even in a well-defined environment and for the same material, this nobility can vary within a wide range.

For instance, consider the classic case of austenitic stainless steel - containing, for example, 18% chromium and 10% nickel with or without molybdenum - immersed in seawater. If the water is aerated, this steel, while it remains in a passive state, assumes nobility not far from that of gold. However, it shifts to the nobility of carbon steel as soon as it starts to corrode. On the other hand, if the seawater contains little oxygen or is even deaerated - as in mud at the ocean floor, or inside an oil reservoir where oxygen was never present or has been consumed, or within a desalinator where oxygen has been intentionally removed, or in a brine saturated with salt where oxygen solubility is virtually null due to high salinity - the potential of this stainless steel decreases by several hundred millivolts, even while it remains in a passive state, reaching the potential of carbon steel. Therefore, in conditions where oxygen is absent, couplings of stainless steel and carbon steel do not induce any corrosion on the latter material.

On the other hand, in conditions where even iron is passive - for example, in alkaline solutions or in concrete - the potential of iron is affected by all factors that change the potential of stainless steel. Consequently, passive iron and stainless steel end up having roughly the same potential, meaning the same practical nobility. In these conditions, couplings of stainless steel and carbon steel also do not cause any corrosion on the latter material, irrespective of whether the environment is aerated or not.

But let's see some... reversals

Materials can indeed change positions in the practical nobility scale. However, unlike politics, these reversals occur only under specific conditions, which can be known in advance. Let's look at some examples.

Zinc is generally less noble than iron, so in this pairing, it corrodes and protects the iron. However, at temperatures above 40°C in water that allows the formation of oxide with specific semiconductor characteristics, zinc can become cathodic relative to iron. In these cases, the zinc-iron pairing causes the corrosion of iron.

A similar discussion can be applied to tin, which is generally cathodic to iron, thus stimulating its attack. However, in contact with oxalic acid or other organic substances that passivate iron, tin becomes anodic. In this case, it is tin that corrodes, protecting the iron. A beneficial reversal, this time, or else we wouldn't have been able to use tin-plated steel for cans of tomato sauce or beans.

The phenomena of adjustment

To predict the effects of their coupling, the practical nobility of metals must be evaluated after the surface adjustment phenomena have occurred in the initial operating periods. These adjustments are related to both the formation of films of corrosion products and the selective attack of some constituents of the materials themselves. Both of these processes can lead to radical changes in composition and, therefore, the electrochemical behavior of the surface.

For example, even if adequately inhibited, brass can undergo surface dezincification, resulting in the production of a slight copper film. As a result, their nobility level, in environments where this happens, becomes equal to that of copper. A similar situation occurs with gray cast irons; graphite exhibits practical nobility even higher than that of stainless steels.

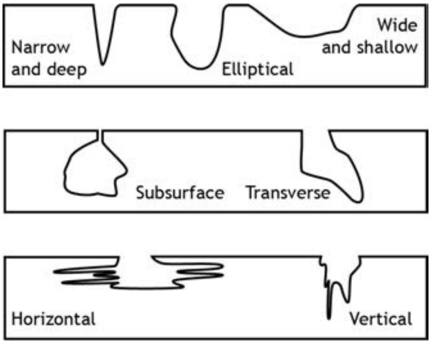
On the other hand, turbulence or abrasive phenomena can locally destroy surface films, leading to a transition from passive to active conditions and thus de-nobilitation of materials that are no longer covered by the films. Consequently, galvanic effects, which are absent under calm conditions, can become non-negligible in the presence of turbulent flows. For these reasons, differences in practical nobility can even develop between two initially identical materials in the same environment.

Pitting is a severe form of localized corrosion

Understanding the mechanism behind this condition, also known as "pitting," is crucial, and it is equally important to be able to assess the materials selection in relation to the operating conditions.

Pitting is a type of localized and penetrating corrosion that creates cavities (pits) with diameters usually less than a few millimeters and varying in number from a few units to many hundreds per square meter. In the past, these cavities were referred to as ulcers, craters, caverns, honeycombing, pinholes, and more, depending on their shape. Today, following the less suggestive terminology of ASTM standards, they are typically described as either wide and shallow, narrow and deep, elliptical, transverse, subsurface, vertical, or horizontal.

The pitting attack is typical of metallic materials covered by passive films, such as iron, copper, aluminum, nickel, and their alloys, in the presence of oxidizing environments and chlorides. In this context, we will mainly refer to the case of stainless steels.



Graphic representation of typical forms of pitting.

Danger of Pitting Corrosion

The danger of pitting corrosion lies in the fact that the depth of the cavities can quickly reach the entire thickness of the metal wall. For this reason, pitting corrosion often leads to the perforation of pipelines or equipment, resulting in significant damage.

In some cases, pitting can also have structural consequences. For instance, in reinforced concrete structures contaminated by chlorides, it can significantly reduce the cross-section and, consequently, the load-bearing capacity of the reinforcements. In tensioned structures or pressure vessels, it can initiate stress corrosion cracking or lead to hydrogen embrittlement.

What makes this type of attack even more dangerous is the statistical nature of its initiation, which leads to its localization not always being identifiable in advance, and its dot-like characteristic, making its presence easily masked by various deposits and escaping careful inspection until it causes irreparable damage.

Even when the attack is shallow and clearly identifiable, it can have significant economic consequences.

This is the case, for example, with surface attacks that occur on elements constructed with stainless steels used in architecture, compromising their aesthetic appearance. It also applies to those that occur on aluminum parabolic reflectors, reducing their reflective power.

The mechanism of the phenomenon

The initiation and development of each individual pit create a circulation of current between two distinct zones on the metal's surface: the area where the attack takes place, tending to assume the form of a cavity (anodic zone), and the surrounding area where the reduction of oxygen or other oxidizing species present in the environment occurs (cathodic zone).

This circulation gives rise to a series of reactions and chemical changes that further stimulate the attack of the zones that are already corroding, i.e., inside the pits, and protect the surrounding cathodic areas. This results in pitting corrosion occurring at an increasing rate, with the tendency to penetrate the interior of the material rather than spreading over its surface.

In particular, within the cavity, there is a significant increase in acidity and an increase in chloride content that the current carries from the external environment. For example, in the case of stainless steels in contact with neutral solutions with only a few grams per liter of chlorides, chloride concentrations ten to a hundred times higher and pH values close to zero can be measured in the pit. Conversely, in the areas around the cavities, the cathodic reduction of oxygen produces an increase in pH, reinforcing the existing passivity conditions.

The corrosion products, which tend to separate at the boundary between the anodic and cathodic zones, often form a kind of cap around the attacked area. While this cap does not prevent the electrophoretic migration of chlorides from the outside to the inside of the pit, it significantly limits diffusive processes in the opposite direction. In such cases, the separation between the external environment and the internal zones, referred to as occluded cells, becomes even more distinct and stable.

The initiation of pitting

In pitting corrosion, two stages are distinguished: the initiation of the pit and its growth. Initiation occurs after a material has been exposed to the aggressive environment for a variable period, ranging from a few weeks to several months, depending on the steel's characteristics and environmental conditions (incubation period). It occurs where the protective surface layer is weak or has defects (for example, in welded areas that may lack passivating elements or are covered with non-protective oxides, in work-hardened zones with structural modifications, at locations with emerging inclusions, and so on). Alternatively, initiation can occur where, due to local increases in temperature or the concentration of aggressive species, the environment becomes more corrosive.

Stagnant conditions reduce the incubation period and, therefore, promote initiation, while agitation or turbulence in the environment hinders it. For example, stainless steel AISI 316 pipes are susceptible to pitting when in contact with stagnant seawater, but they are not corroded if the water velocity exceeds 1.5 m/s.

Another important aspect of initiation is illustrated by the following example related to stainless steel pots.

In theory, the environment they come into contact with, containing chlorides, oxygen, and characterized by high temperatures, could initiate pitting corrosion on the austenitic stainless steels like AISI 304, which are commonly used to make pots. In practice, initiation does not occur because, given an incubation period on the order of months, the actual contact duration is only a few hours or at most a few days, as the pitting process starts from scratch every time the pot is washed (provided there are no encrustations or deposits on the steel's surface, and no metallurgical defects or cracks are present).

Similar considerations apply to explain why the resistance to pitting of batch reactors, used in the chemical or food industries and essentially operated in the same way as pots, is much greater than that of continuous reactors operating in the same environmental conditions.

The propagation of pitting

Once the attack has initiated, its propagation is extremely rapid and can, for example, lead to perforation of several millimeters' thick walls within a few months. Agitation, which is beneficial in preventing the attack, accelerates it once initiated.

When pitting has penetrated deeply into the material, it is very difficult to stop. In the case of stainless steels, washing with chloride-free alkaline solutions, such as sodium carbonate-based solutions, can only halt the attack if its penetration is modest, for example, less than 0.5 mm. Otherwise, only drastic and often practically unfeasible and costly interventions that can mechanically remove the corroded area are effective.

It is evident, therefore, that pitting is best fought through proper material selection and control of the environment to prevent its initiation. Thus, practical knowledge of the electrochemical, metallurgical, and environmental conditions in which such attack occurs is of great importance.

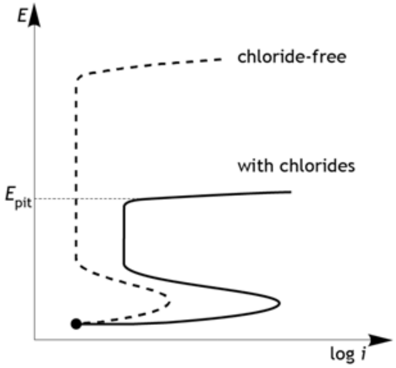
The initiation conditions

Stainless steels undergo pitting attacks only in the presence of specific ions. In the vast majority of cases, these ions consist of chlorides. However, bromides (but not fluorides and iodides), hypochlorites, sulfides, and thiosulfates in particular conditions can also cause the attack.

Let's consider the most important case where the attack is caused by the presence of chlorides.

These anions reduce the range of potentials within which stainless steel is passive. More precisely, they lower the upper limit of this range, which is called the pitting potential (E_{pit}).

Above this potential, the protective film is brocken, making the initiation of the corrosion process possible. Therefore, pitting attack can only occur if the potential to which stainless steel is exposed when it comes into contact with the aggressive solution (usually denoted as E_{corr}) is higher than the pitting potential, meaning only if $E_{corr} > E_{pit}$. Conversely, it does not initiate if the opposite condition is verified, meaning if $E_{corr} < E_{pit}$.



Typical behavior of the anodic characteristic curve of stainless steel showing the influence of chloride presence and identifying the pitting potential.

It is evident that as E_{pit} decreases, the range of oxidizing power in which stainless steels can operate also decreases, moving to lower values. On the other hand, as E_{corr} decreases, the group of stainless steels that can resist expands to less resistant types. Once the attack has initiated, it can also progress at potentials lower than E_{pit}. To stop it, it is necessary to reach the protection potential, typically 300 mV more negative than the pitting potential.

The corrosion potential

The corrosion potential (E_{corr}) to which stainless steel is exposed (before it is potentially attacked) primarily depends on the oxidizing power of the solution it comes into contact with. Therefore, it increases with the concentration of oxygen or other oxidizing species that may be present, such as chlorine, ferric ions, cupric ions, and others. In seawater at temperatures below 32-40 °C, the presence of bacterial activity leads to the formation of a surface film on stainless steel made up of biological substances, known as the biofilm, which catalyzes oxygen reduction and increases E_{corr} by several hundred millivolts.

Of course, E_{corr} increases when stainless steel comes into contact with materials characterized by higher potentials, such as graphite, or when it exchanges anodic current (i.e., from the steel to the environment). Conversely, it decreases when in contact with less noble materials like zinc, aluminum, or carbon steel, or when an external current is imposed on the material (as is the case of cathodic protection).

Seawater provides a good summary of the concepts discussed so far. When deaerated, the E_{corr} of stainless steel (before any potential attack) is about -0.5 V (relative to the standard calomel reference electrode, SCE). If there is no bacterial activity, such as in synthetic or sterilized seawater, it's approximately 0 V. However, in the presence of bacterial activity, typical of all-natural seawater, it's about +0.4 V SCE. If seawater contains chlorine at concentrations ranging from 0.5-1 ppm because it has been treated to remove its biological charge, as is common in the oil industry, the potential can even reach +0.6 V. If stainless steel in seawater is coupled with iron, E_{corr} drops below -0.4 V; if coupled with zinc or aluminum, it may even fall below -1 V. Similarly, extremely negative values can be achieved when stainless steel is subjected to a cathodic current by an external DC generator, regardless of whether the water is natural, deaerated, sterile, or chlorinated.

The pitting potential

The pitting potential (E_{pit}) depends on both the composition and structure of stainless steel and the nature, composition, and temperature of the surrounding environment. Concerning the steel's composition, E_{pit} increases with higher chromium, molybdenum, nitrogen, and tungsten content, while it decreases with increased sulfur and manganese content. Regarding the environment, E_{pit} decreases with higher chloride concentration, acidity, and temperature. Some ions, like acetates, sulfates, or perchlorates, counteract the negative influence of chlorides, while others, such as sulfides and thiosulfates, facilitate it.

Critical Temperatures and Critical Chloride Content

To compare the behavior of different materials under specific environmental conditions or the behavior of one material under varying conditions, critical temperature and critical chloride content are often used. These parameters represent the extreme conditions of temperature and chloride content at which each material can resist attack (assuming all other environmental and potential conditions remain constant).

To provide some examples of critical temperature, consider steels in a 6% ferric chloride solution (commonly used as a test solution to compare the behavior of different steels). In this environment, the critical temperature is as follows: 0 and 20°C for AISI 304 and AISI 316, 75°C for the superaustenitic 254 SMO (a steel with high chromium and molybdenum content), and 100°C for the even more resistant 654 SMO. This means that the listed steel types do not corrode in a 6% ferric chloride solution below the indicated temperatures.

As for critical chloride content, let's consider the case of concrete exposed to the atmosphere and contaminated with these anions. In this environment, the critical chloride content is approximately as follows (expressed as a percentage by weight relative to cement): 0.5% for carbon steel, 1.5% for galvanized reinforcement, 2% for ferritic stainless steels like AISI 430, 5% for AISI 304 stainless steel, and 8% for AISI 316 stainless steel (although these last two values drop to 3.5% if the steels are welded without removing the oxides formed in the heat-affected zone). Recent data indicates that the reinforcement made of austenitic stainless steel AISI 304 and 316 is not susceptible to pitting, even in concrete exposed to the worst chloride contamination encountered in practice.

Pitting Resistance Index

To assess the pitting resistance of stainless steels, the *Pitting Resistance Equivalent Number* (PREN) is often used. The PREN increases with higher pitting resistance and is defined as follows: PREN = %Cr + 3.3·%Mo + x·%N, where x is zero for ferritic steels, 16 for austenitic steels, and 30 for duplex steels.

The PREN only considers the influence of steel composition (specifically, the main elements) but does not take into account the crystal structure, surface conditions, or the presence of inclusions. For example, the use of steels with a PREN of 18 or lower (including AISI 304) is recommended in the presence of low chloride concentrations, namely lower than few hundreds of ppm, depending on temperature, pH and fluid dynamic conditions. They can also be used at high pH levels, such as in concrete with a pH of 13.

Steels with a PREN of at least 26, including AISI 316, can be used in contact with brackish water with chloride concentrations not exceeding a few grams per liter, provided the water is not acidic and the temperature does not exceed 20°C. These steels do not pit in a marine atmosphere, physiological saline solution, or in the human body. Seawater can cause pitting on these materials even at typical temperatures of cold seas. Typically, steels in this group are cathodically protected by galvanic couplings with carbon steel, zinc, or aluminum anodes in this environment.

Steels with a PREN above 40 do not experience pitting in seawater unless coupled with carbonaceous materials, subjected to anodic polarization, or the water has undergone chlorination. In the latter case, to eliminate the possibility of pitting corrosion, it's necessary to use steels with a PREN above 50 (such as superaustenitic or superduplex steels, e.g., 254 SMO with 6 molybdenum or 654 SMO with 7 molybdenum).

It's important to note that when choosing materials, consideration should be given to all forms of localized corrosion, not just pitting. In particular, stress corrosion cracking, which has a mechanism similar to pitting, can occur under less severe conditions than those causing pitting corrosion.

Different Stress Corrosion Situations

For now, let's take an overview of the phenomenon that, due to the combination of various factors, can be the source of severe structural failures.

The simultaneous action of particular environments that are inherently not very aggressive or even completely non-aggressive, along with a tensile stress state characterized by stress levels lower than those required to cause purely mechanical failure, can lead to the formation of cracks within certain materials, which can result in their failure. This phenomenon is called *stress corrosion cracking* and falls under the category of environmentally assisted cracking or *environmentally induced (or sensitive) cracking*, along with fatigue corrosion and hydrogen embrittlement.

In the past, this phenomenon has been given specific names based on the conditions and materials in which it occurs, such as caustic embrittlement of carbon steels, season cracking of brass, nitrate cracking, hydrogen cracking, liquid metal embrittlement, and others.

Season cracking of a tin-plated brass coffee pot kept in a humid atmosphere saturated with ammonia. The internal stresses that caused the attack, resulting from the lack of post-forming stress relief, are combined with the effects of the humid environment and ammonium salts present in gunpowder. This phenomenon was named "season cracking" by British military personnel stationed in India at the end of the last century because the attack primarily occurred during the rainy season. The combination of the humid environment, ammonium salts in gunpowder, and residual internal stresses from the manufacturing process contributed to this type of failure, which also occurred during World War II..

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A highly dangerous form of attack

The fact that failures caused by stress corrosion cracking often occur without any warning makes this type of attack extremely dangerous. Literature contains numerous cases of structural collapse or severe damage. As an example, for carbon steel, there have been instances of boiler explosions and chemical equipment failures in environments containing nitric acid, caustics, or specific types of soils. For high-strength ferritic steels, failures have included the collapse of support hooks, cables, reinforcement bars, or structural elements in contact with aqueous environments. Stress corrosion cracking has also affected tubing in sour oil wells.

Concerning stainless steels, equipment used in chemical or petrochemical environments containing chlorides or in caustic environments has been rendered inoperative. Nuclear reactors of the pressurized water reactor (PWR) type have been affected by stress corrosion cracking due to water exposure at 280°C. Copper and aluminum alloys have experienced failures in contact with ammonia or hydrochloric acid solutions, respectively.

In every case, stress corrosion cracking occurs only under specific combinations of metallic material and environment. For example, austenitic stainless steels can experience stress corrosion cracking in chloride or caustic environments but not in ammonia or nitric acid environments. Carbon steels are prone to stress corrosion cracking in nitric or caustic environments but not in chloride or ammonia environments. Copper alloys may corrode in ammonia-rich environments but not in chloride-rich ones.

Unfortunately, for certain materials like high-strength steels, the chemical species that can cause stress corrosion cracking is pure water. In this case, the specificity of the environment is not of significant practical relevance.

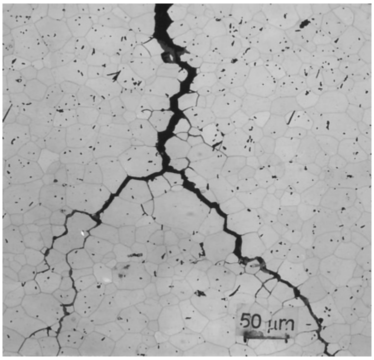
Metallic materials are susceptible to stress corrosion cracking not only in aqueous environments but also in organic solutions, molten salts, liquid metals, gaseous atmospheres, or beneath salt crusts. For instance, titanium can undergo cracking in methanol, under a hot sodium chloride crust, or in an azide atmosphere.

Moreover, non-metallic materials can also experience forms of environmentally assisted cracking. Many polymers, including polyethylene or natural and synthetic rubbers, can crack under the combined action of mechanical stress and non-solvent environments.

Morphology and initiation conditions

Failure caused by stress corrosion cracking often occurs without significant plastic deformation in the metal, giving the misleading impression that the material that failed is intrinsically brittle while it possesses normal ductility characteristics.

Cracks tend to propagate perpendicular to the direction of the maximum tensile stress. Depending on the metallic material, the environment, the magnitude and distribution of stresses, the cracks can be primarily intergranular or transgranular and more or less branched. For example, austenitic stainless steels exposed to chloride-containing environments exhibit branched transgranular cracks with the typical appearance of a river delta. In a caustic environment, intergranular cracks, generally non-branched, may occur. However, even with various metal-environment combinations, a predominantly intergranular or transgranular crack pattern, the transition from one type of fracture to another can occur due to variations in applied stress levels, the structural conditions of the metallic material, the chemical composition of the environment, temperature, or the testing methodology itself.



Intergranular Stress Corrosion Cracking of a U-bend sample of ferritic stainless steel (21 Cr - 3 Mo) held for 500 hours in a solution of NaOH (200 g/L) and NaCl (10 g/L) at 280 °C.

The initiation of cracks

In the process leading to stress corrosion cracking, two stages can be identified: an initial incubation stage or initiation of cracks, and a second stage of crack propagation, potentially leading to conditions where there is mechanical failure of the material.

The environment itself can be capable of nucleating stress corrosion cracking. In this case, crack initiation can occur on the material's surface, which is free from irregularities in shape or macroscopic defects, starting from imperfections or gaps in the protective film. These imperfections are often found in areas with metallurgical defects, particularly at emerging inclusions or in zones with tensile stress in the oxide due to the emergence of slip bands. Crack initiation can also occur at grain boundaries or at the interface between different phases, where the material exhibits increased inherent susceptibility to corrosion.

Naturally, the presence of macroscopic stress concentrators on the material's surface, such as notches, fillets, holes, keys, or defects like folds or welding defects, promotes the initiation of the attack.

The incubation time depends on the chemical composition of the material and the aggressive environment. It is influenced by parameters like salt concentration, pH, oxygen content, other oxidizing species, potential, temperature, as well as the magnitude of the applied stresses and their variations over time.

In practice, the incubation time can vary from a few minutes to several years, depending on the combination of material/environment. For example, austenitic stainless steels in boiling magnesium chloride may show signs of cracking in just a few hours of immersion. On the other hand, nickel-based superalloys used in PWR nuclear reactor primary loop components, exposed to high-temperature water (280°C), often exhibit incubation times on the order of several years.

In general, even for a well-defined material/environment combination, measurements of the incubation time exhibit significant variability due to the fluctuations in all the aforementioned factors. This variability is not negligible, even in the most controlled laboratory tests and is even more pronounced in real-world operating conditions.

The aggression increases with other forms of corrosion

Sometimes, the environment is not capable of promoting stress corrosion cracking phenomena, but it becomes so only after a localized increase in aggressiveness. This localized increase often occurs within localized corrosion attacks like pitting or crevice corrosion.

As is known, such forms of corrosion create what are called occluded cells within the corroded areas. These cells have an environment that is entirely different from the external one, with much higher concentrations of anions and hydrogen ions, an absence of oxygen, and, as a result, lower potentials.

This explains why crack initiation often occurs at locations where crevice corrosion is promoted, such as at points of local exposure that are shielded or occluded. These points can result from deposits, scaling, surface folds, welding defects, capillary gaps between inclusions and the matrix, plate-to-plate, plate-to-tube, tube-to-diaphragm junctions, gaskets, insulating shields, joints, supports, spacers, and more.

In these cases as well, the initiation time depends on the metallurgical, mechanical, electrochemical, and environmental parameters mentioned earlier for crack initiation in the general case. Additionally, it depends on factors that lead to local increases in aggressiveness, linked to the geometry of the crevice, the agitation conditions of the environment, or its tendency to deposit or keep deposits in suspension.

Crack propagation

Once a crack has initiated, its propagation occurs due to the combined action of the corrosive environment and applied stresses. The rate of crack propagation depends on the characteristics of the environment, the metallic material, and the stress state. In general, the crack propagation rate falls within the range of 10^{-11} to 10^{-6} m/s, which means it can vary from penetration rates that are barely noticeable to very high values. For instance, in the upper-middle part of this range, where crack propagation rates are significantly greater than a millimeter per year, you find austenitic stainless steels in contact with acidic hydrochloric solutions, copper alloys in ammonia solutions, and carbon steels in nitrate environments. In the lower-middle part of the range, with propagation rates on the order of tens of microns per year, you would find nickel superalloys (like alloy 600) used in pressurized water reactor (PWR) nuclear plants in contact with water at 280°

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Stress corrosion cracking in the handle of a shaving brush made of a zinc-aluminum alloy. The advancement of the crack was monitored by the author every morning for four years. The stress state was induced in the metal part by the swelling of the central wooden core. This case illustrates one of the most subtle aspects of stress corrosion cracking, namely, the fact that it can occur in some materials – a typical example being lightweight metal alloys containing specific impurities in excessive amounts or subjected to incorrect heat treatments – even in environments that appear to be slightly aggressive or entirely harmless.

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Structural Failures and Reinforcement Corrosion

Reinforcement corrosion has often been the cause or a contributing factor to structural failures in reinforced concrete (RC) and pre-stressed reinforced concrete (PRC) structures. In the vast majority of cases, this phenomenon was made possible by the poor quality of the cementitious material, inadequate or even locally missing concrete cover, imaginative construction details, lack of maintenance, and ultimately, by errors or negligence in the design, construction, or management of the structure. These situations are mainly found in buildings constructed from 1950 to 1975, a period when nobody was concerned about the durability of the structures being built. It was not uncommon to use inadequate concrete, not only in absolute terms but also in relation to the common practice at the time, which frequently involved using smaller pillar sections as a cost-saving measure for the builder and as a test of the designer's skill.

Unfortunately, severe corrosion-related situations continue to occur in structures completed after 1975. For instance, in the industrial port of Manfredonia, which was approved in 1979, corrosion is heavily affecting not only the outer reinforcement but has already led to the failure of several pre-stressed cables. Similarly, in residential buildings in Molfetta, handed over to the owners in the late 1990s (yes, you read that correctly!), the extent of corrosion damage was so severe that some units have required evacuation (with partial evacuation already completed). (*This article was originally published in 2003.*)

It should be noted that even well-designed and constructed reinforced concrete (RC) and pre-stressed reinforced concrete (PRC) buildings are not eternal, as was commonly believed until the 1970s. Their service life is limited by the corrosion of the reinforcements. However, if the environment does not contain chlorides, there are no difficulties in designing structures with a service life of up to 75-100 years, or perhaps even longer, especially in temperate climates. In cases where these ions are present, such as in marine structures or bridges where de-icing salts are used, the risk

Port of Manfredonia: generalized corrosion of reinforcements and stress corrosion cracking (SCC) of high-strength reinforcements.

of corrosion attacks in the most stressed parts can be avoided for only about thirty to at most forty years. To ensure longer service lives, it is necessary to use special additional protections, such as corrosion-resistant reinforcements, cathodic prevention, coatings, inhibitors, and more.

To address the issue of structural failures caused by corrosion, it is necessary to begin with some general considerations about corrosive phenomena in concrete. These considerations have reached a good level of understanding since the 1990s.

Corrosion in RC and PRC structures

In alkaline solutions with a pH greater than 11.5 and in the absence of chlorides, iron is covered by an extremely thin protective oxide film, only a few nanometers thick. In these conditions, known as passivity, the corrosion process does not occur. Concrete, in its interaction with the reinforcements, behaves as an alkaline solution, effectively protecting them. Unfortunately, over time, concrete can lose this property as a result of carbonation, which is the neutralization reaction of the solution in the capillary pores of the concrete by atmospheric carbon dioxide, or due to the penetration of chlorides, typically from de-icing salts or seawater. The destruction of the protective film, occurring primarily due to carbonation throughout the surface of the reinforcements reached by carbonation and locally due to chloride penetration, is the precondition for corrosion to take place. To initiate corrosion, the presence of water and oxygen is also required.

In the life cycle of reinforced concrete structures, two clearly distinct phases can be identified: the initiation phase of corrosion, during which the processes leading to the destruction of the protective film occur; and the propagation phase of the attack, which begins when the film is destroyed and continues until corrosion causes unacceptable damage. The initiation time mainly depends on the characteristics of the concrete and the thickness of the concrete cover, while the propagation period depends on the corrosion rate, which is in turn related to the water content of the concrete and the presence of chlorides.

Carbonation: Carbonation follows a parabolic law, which is given by the formula $s = k \sqrt{t}$, where s is the depth of the carbonated layer, t is the time, and k is a coefficient that depends on concrete properties and environmental factors. Corrosion due to carbonation occurs at a high rate in environments characterized by high relative humidity or wet-dry cycling.

If chlorides are present in carbonated concrete, even in concentrations much lower than those required to initiate corrosion in alkaline concrete, things change. In this case, corrosion also occurs inside buildings.

Chlorides induced corrosion: Chlorides can induce the corrosion of reinforcement when their concentration exceeds a certain threshold. In practice, the risk of corrosion is low for chloride content at the surface of the reinforcement below 0.4% (by mass relative to the cement content) and high for concentrations exceeding 1%. In the majority of cases, chlorides come from external sources. The corrosion initiation period, which is the time required for chlorides to diffuse through the concrete cover and accumulate at the reinforcement surface to reach the critical value, depends on the surface chloride concentration, concrete characteristics, and the cover thickness. Chloride attack is localized and penetrating, and with the potential to reach corrosion rates of several hundred micrometers per year, it can lead to unacceptable reductions in the cross-sectional area of the reinforcement within a few years. To counteract this, action should primarily focus on the initiation time by using concrete with low porosity and chloride permeability and sufficiently thick cover layers of reinforcement.

Hydrogen embrittlement. Metals under specific metallurgical, environmental, and loading conditions can be subject to corrosive phenomena that cause cracks in the material, known as Stress Corrosion Cracking (SCC). SCC phenomena occur only in the presence of specific material metal/environment couplings. Unfortunately, in the case of high-strength steels, one of the environments that can cause embrittlement is water, particularly rainwater, if it remains in prolonged contact with the steel inside confined areas, enclosed spaces, or improperly injected sheaths.

In concrete, the typical mechanism of SCC is hydrogen embrittlement. This doesn't occur if the reinforcements are covered with alkaline concrete and free from chlorides. However, it can occur in the presence of defects or gaps in the concrete, or where carbonation or chlorides have destroyed the passive conditions. If the amount of hydrogen and tensile stresses are sufficiently high, and the material is susceptible to hydrogen embrittlement, cracks form in these areas, advancing until material fracture occurs.

The structural consequences of corrosion

The corrosion of reinforcement leads to a progressive reduction in the safety margins on which structural design is based. Firstly, it causes a decrease in the effective cross-sectional area of the reinforcement, resulting in a reduced capacity to withstand static or dynamic loads. In particular, the corrosion of stirrups, which are the first to be affected by the depassivating action of carbonation or chlorides, can compromise their confinement capacity, thereby destabilizing the primary reinforcement.

Corrosion generates oxides that occupy a much greater volume compared to the original iron and can cause cracks in the concrete cover, even leading to spalling or delamination, reducing the effective cross-sectional area of the concrete. Finally, under specific conditions, it can produce atomic hydrogen, which can trigger brittle fractures in susceptible hydrogen embrittlement-prone steels.

Let’s now consider the corrosive aspects of some structural failures to highlight the concerning level of vulnerability that reinforced concrete or prestressed concrete structures may acquire over time when subject to corrosion.

The collapse of the building on Via Pagano in Palermo (1999)

At 7:40 PM on March 11, 1999, a six-story building constructed in 1969 on Via Pagano in Palermo collapsed. Starting from 7:00 PM, there were clear signs of structural failure, such as shattered windows, wall cracks, noises, and door frame breakages. As a result, all the tenants evacuated the building, except for two elderly residents living on the upper floors who were unable to break down the jammed security door, and a firefighter who was attempting to rescue them.

Upon the initial visual inspection of the debris, significant oxidation of the reinforcement surfaces was observed. As a result, the technical committee appointed by the Prosecutor’s Office was expanded to include corrosion and materials experts. The conducted investigations revealed that the collapse had been triggered by the failure of one or more basement pillars, which were found to be: undersized, constructed with low-quality concrete, severely weakened by corrosion, and some of them had undergone belated extraordinary maintenance work in an attempt to remedy the damage caused by corrosion, which had been evident for over a decade. (The request for extraordinary maintenance work on parts of the basement in precarious condition had been on the agenda of the condominium assembly since 1991. However, disputes within the assembly, leading to a series of legal challenges, prevented its timely execution)

Collapse on Pagano Street in Palermo: basement pillar near those that triggered the collapse.

Geotechnical investigations, on the other hand, ruled out any correlation between the building's collapse and the foundation substrate..

Concrete analysis of the basement pillars indicated that the concrete used had low cement content and high water-cement ratios, resulting in a highly porous, weak, and less durable material. The concrete also showed the presence of chlorides distributed throughout the cementitious mass. This suggests that chlorides had been introduced into the mix during construction, likely through sand taken from near the sea without proper washing. Their content was relatively modest and generally below the critical threshold to initiate corrosive processes in alkaline concrete but sufficient to cause corrosion in the carbonated concrete of the basement of the building. The thickness of the concrete cover for the reinforcement was found to be adequate.

Corrosion Analysis. The concrete cover of many basement pillars exhibited cracks and, in extensive areas, especially in the lower part, delamination. Carbonation had penetrated the concrete to varying depths, well beyond the stirrups and main reinforcement. On the reinforcement, particularly in their lower parts, a widespread and uniform corrosion attack was observed, typical of carbonation-induced corrosion, resulting in a reduction in the diameter of the main reinforcement bars.

The stirrups showed thinning and a consequent reduction in their cross-sectional area. There were layers of corrosion products, several millimeters thick, in the most corroded areas of the reinforcement. Some pillars had their effective cross-sectional area reduced by 25% to 30% due to the detachment of the concrete cover.

Outside the areas that had triggered the collapse, sporadic localized attacks, such as pitting corrosion, were also observed, likely caused by the presence of chlorides. In these cases, the chloride content in those areas evidently exceeded the critical level, resulting in reductions in the cross-sectional area of some reinforcement bars, in some cases up to 50%.

Some Assessments. The temporal development of corrosion phenomena in the basement pillars was reconstructed. Carbonation had reached the main reinforcement after approximately 11 years, suggesting that corrosion on the reinforcement had likely commenced in 1980. The corrosion rate was estimated to be at least 25 μm per year, significantly higher than what is typically observed inside buildings due to the action of chlorides in carbonated concrete. It could be deduced that the complete loss of bond between the reinforcement and concrete and the formation of initial microcracks around the reinforcement in the concrete occurred around 8 years later, in 1988.

Similarly, for the stirrups, a time of initiation of around 8 years was estimated, suggesting that their corrosion had even started as early as 1976.

The collapse of the Ponte di Santo Stefano Bridge near Taormina (1999)

On the night of March 23, 1999, less than two weeks after the collapse of the building on Via Pagano in Palermo, near Taormina, where State Road 114 runs approximately 50 meters from the sea, the Ponte di Santo Stefano Bridge collapsed. It happened without any prior warning, without overloading the bridge in any way, and, fortunately, without any vehicles involved and, thus, without casualties. Due to this, the national press practically didn’t report it. The bridge was a prestressed structure obtained by joining precast concrete elements on-site. Prestressing was applied in the final phase of construction by inserting high-strength steel tendons into 40 mm diameter ducts formed by drilling holes through the concrete elements. The bridge, designed by Morandi, was built in 1954. It consisted of four spans with a length of 18.50 m, for a total length of 78 m and a width of 12.50 m. Due to its location, the east side of the bridge was often exposed to strong onshore winds from the sea.

Initial investigations immediately revealed that at least some of the ducts housing the high-strength steel tendons, consisting of 5 mm diameter steel wires, had not been properly filled with cement grout; in some sections, the filling was completely absent. However, the tendons showed modest signs of corrosion, except in areas on the sea side, where the concrete cover had reached minimum values, was contaminated with chlorides, and exhibited longitudinal cracks, especially at the joints between the precast concrete elements. In these areas, corrosion had significantly reduced the cross-sectional area of the tendons, to the point of complete destruction in some places.

The concrete cover for the tendons in the stressed area was of good quality but exhibited non-uniform thickness due to the misalignment of the tendon ducts.

Laboratory analyses ruled out the presence of cracks in the reinforcements, thus eliminating the hypothesis of stress corrosion cracking due to hydrogen embrittlement, which should be considered for high-strength steels.

From the previous analyses, it was evident that the causes of the collapse could be traced back to construction errors, which were unacceptable in a structure designed to operate in the vicinity of the sea. These errors included misaligned ducts leading to localized reductions in the concrete cover, partial or even total lack of grouting, improper sealing of joints, and the absence of maintenance and inspections.

Several considerations can be drawn from this. Firstly, prestressed concrete bridges are more vulnerable to corrosion-induced failures due to the difficulties in maintaining the tendons over time, especially in the region of the joints between the various elements and anchorages. In fact, following the collapse of Ynys-y-Gwas in 1985 and other critical situations involving the corrosion of tendons at the joints of bridges, the UK Department of Transport prohibited new constructions of this type in 1992. The ban was lifted in 1996 for in-situ cast structures but still applies to precast concrete elements. Such restrictions, however, are not considered necessary in other countries. Furthermore, construction of this type of bridges has been prohibited by the *Japan Highway Public Corporation*, the body that controls most of Japan's highways, in recent years.

Secondly, structural enhancements for aesthetic purposes have often led to catastrophic failures induced by corrosion. For instance, the unexpected collapse of the bridge over the Schelde River in Belgium in 1992, with tragic consequences, occurred due to a construction detail intended to make the structure more elegant. In the pillars, an incision was made to enhance the structure's appearance, which inadvertently allowed chloride retention from the deck, localized reduction of concrete cover, and corrosion of the high-strength reinforcement beneath, ultimately leading to the collapse. These are the types of corrosion-induced failures that Peter Schiessl calls SIC (*Stupidity Induced Cracking* or, if you prefer, *Stupidity Induced Corrosion*). There are also those who, perhaps in an attempt to surpass Ictinus and Callicrates, design bridge pillars inspired by the fluted columns of the Parthenon. Others prefer transverse incisions. They may not be aware that any groove or incision that reduces the concrete cover, for example, by 25%, practically halves the time for the initiation of carbonation-induced corrosion, and if the structure is contaminated with chlorides, the service life is halved.

The third consideration relates to additional protections. In cases of extensive use of anti-icing salts or in the most critical areas of marine structures, avoiding errors is often insufficient to ensure sufficient reliability for the entire intended service life. Sometimes, especially for the most stressed parts, it may be necessary to resort to additional protective measures, which often require more monitoring and maintenance than the structure itself. Some of them also require activation. I recall, in this regard, that in the late 1980s to early 1990s, on over 120,000 square meters of new viaducts and highway bridges, especially in alpine regions, constructed with precast prestressed concrete elements, the so-called cathodic prevention was installed. This was done officially to "make durable expensive structures, minimize maintenance costs, and eliminate the high social costs resulting from construction sites disrupting traffic on active roadways." However, in reality, it was also to reduce the vulnerability of the tendons in the joint region between the elements. The costs for this were far from trivial. (*The application criteria for this technique were defined in the early 1990s by Pietro Pedeferri and have since been incorporated into international regulations. The diagrams illustrating these criteria are now known as Pedeferri Diagrams.*)

The increase in reliability achieved through this innovation was advertised for a long time. However, in the vast majority of cases, the systems prepared for prevention, even though ready to operate at the time, were not activated, perhaps to avoid management complications, or maybe because there is a culture of prevention typical of the civil engineering world, which struggles to see constructions as works that, in aggressive environments, worsen their properties over time and therefore require competence and care in the design and construction phases, but also monitoring and control in the subsequent phases of managing the structure.

In conclusion, I leave the reader with one last consideration, which is also related to the previous point. Once you have read the following two points taken from the conclusions of presentations by American and Canadian delegates at the previously mentioned durability conference. The first point: "The regulations have been improved, now the challenge is to have qualified personnel and educate them." The second point: "Designers should receive more in-depth education on durability, both during university courses and as part of lifelong learning programs."

The Berlin (1980) and Zurich (1985) Collapses

In the 1980s, two structural collapses caused by Stress Corrosion Cracking (SCC) particularly shocked the public and the expert community.

The first incident occurred on May 21, 1980, when a part of the roof of the Congress Hall in Berlin suddenly and without any prior warning collapsed. This building, a gift from the United States to the city divided by the wall, was constructed using reinforced and prestressed concrete. Construction began in 1957, and it was inaugurated in 1961 by President Kennedy during his famous visit to Berlin in the

Congress Hall in Berlin after the collapse.

midst of the Cold War. Fortunately, the collapse happened at night when the building was closed to the public, resulting in only one fatality. The investigation revealed that the collapse occurred due to the brittle fracture of some prestressing tendons that were quenched and tempered (i.e., of the more susceptible type) in the joint region between the precast panels forming the roof and the oval-shaped reinforced concrete ring to which they were anchored. The process that led to the rupture was reconstructed as follows. In a matter of a few years, the protective concrete cover of the sheaths, which had cracked and become permeable, underwent a rapid carbonation process.

The subsequent corrosion of the steel sheaths allowed water to penetrate inside them. The tendons were housed within these sheaths, partly protected by an incomplete layer of concrete and partly by a bituminous coating. This led to the initiation of Stress Corrosion Cracking (SCC) in these tendons and their propagation, ultimately resulting in the collapse of the structure. This event was particularly striking not only because of the significance of the building, which had often been cited as a model for new pre-stressed constructions but also because a crowded concert had taken place in the building just a few hours before the collapse.

The second incident occurred in Zurich in 1985, leading to the collapse of a 200-ton reinforced concrete false ceiling in a swimming pool that had been constructed 13 years prior. This incident resulted in 12 fatalities and many injuries. The false ceiling

Collapse of the ceiling of the Zurich swimming pool.

was suspended from the roof using stainless steel tendons made of AISI 304, which had been cold-worked to increase their strength. The cause of the collapse was identified as SCC in the tendons, occurring where these tendons emerged from the concrete (nothing would have happened if they had been completely embedded). Analysis of the tendons in the vicinity of the fractured area revealed the presence of numerous branching cracks, within which the presence of chlorides was readily detected.

To understand the causes of this collapse, it is necessary to remember that the swimming pool was reserved for disabled individuals three days a week. During these three days, the water temperature was maintained at 37°C. For the rest of the week, the temperature was reduced to 27°C. On the days when the water was at 37°C, there was a significant evaporation of the chlorine used to disinfect the water.

This evaporated chlorine would then condense above the false ceiling, on the surface of the tendons, and accumulate at their base, in the area where they contacted the concrete, leading to the formation of chlorides and hypochlorite. It was in this location that the cracking occurred.

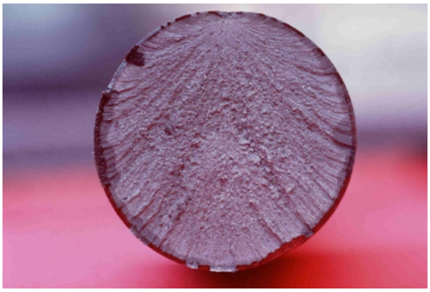
The Incident at the Milan Fair (1997)

On New Year's Day in 1997, in the newly constructed exhibition pavilions at the Milan Fair nearing completion in the Portello area, a sudden and unanticipated failure occurred. A high-strength steel support bar for the floor slabs on the top level broke, causing a 400 m^2 plate to tilt dangerously. In the days that followed, a second bar, and then a third, suffered the same fate as the first. At this point, the seriousness of the phenomenon became apparent and was even reported in the local press. The Milan Fair Authority swiftly took action and secured all the slabs at risk with a massive shoring operation. They subsequently replaced all 800 bars, this time with an added layer of protection: a special coating for the bars and filling the sheaths with wax.

The bars had been left unprotected inside the unsealed sheaths for nearly two years, allowing them to fill with rainwater. Superficial and generally harmless corrosion had developed on their surfaces. However, several microcracks that were prone to hydrogen embrittlement had also formed, and the largest of these soon deteriorated into an unstable crack, leading to the catastrophic failure.

The direct damages, related to the costs for shoring the floor slabs and replacing the bars, amounted to several billion old Italian lire. The indirect damages, resulting from the delay of more than six months in the use of the building and the penalties for canceled exhibitions, amounted to several tens of billion lire. Not to mention the damage to the reputation. Fortunately, the failure did not result in any casualties.

Some questions with an appendix. Fortunately, as mentioned, the collapse did not result in any casualties. However, people wondered, not without some shivers: “What could have happened if the rupture of the bars had not occurred a month and a half before the inauguration of the new pavilions when the structure was still empty and not loaded, but after the inauguration with the halls crowded by thousands of visitors and the roof of the building, used as a parking lot, full of cars?”



Failure of high-strength bars at the Milan Fair: fracture section of a bar. The small area where corrosive processes created the initiation is visible at the top.

And then: “Is it possible that such a failure could happen in such an important work designed by famous engineers, with continuous on-site inspections by prestigious experts, supervised by qualified site managers, constructed by internationally renowned companies? Is it possible that a German company, a world leader in its field, could market bars that a millimeter-sized crack from corrosion can cause to collapse when the applied stress is still far from yielding?” It is possible, it is possible. Or rather, it was possible. So much so that it happened.

There’s still a part of the story worth telling, and since the incident didn’t end in tragedy, we can tell it with a touch of humor. We left off where all the eight hundred bars at risk had been replaced with new ones, protected, and their sheaths were carefully sealed. And so, concerning the pavilions, there were no more issues. But for an external bridge, things went differently. In fact, the following year, around mid-June, one of the supporting bars of the three-level footbridge connecting two pavilions at the Fiera by crossing Viale Teodorico broke just like the previous ones. This time, the fracture didn’t make headlines, except for the annoying traffic disruption that had to be stopped for a few days. However, it activated the officials at the Portello, perhaps already a bit tense, who immediately installed two powerful shoring systems on each side of the footbridge, made of carbon steel beams (“Enough with materials that can cause hydrogen embrittlement!” they must have said), well anchored right in the middle of the pavement below, thanks to concrete casts that were not exactly inconspicuous.

Their purpose was to support the footbridge in case of need and thus make it durable and safe. The aesthetic choice of the designer, who had foreseen three suspension bridges rather than shoring, was clearly penalized. But it was time for someone to prioritize safety and durability over aesthetic preferences! Anyone passing through Via Teodorico can still see these props with their bright yellow beams. It almost seems as if they wanted to give them maximum visibility. Right! In the end, they provide the footbridge with the certainty of remaining intact and prove that the corrosion, like the God, works in mysterious ways. And they are the symbol of how too often safety and durability issues are addressed. That is, they are initially ignored or nearly so. Then, when they become evident, people try to patch them up in some way. Or rather, shore them up. That is, as long as the irreparable hasn't already occurred.

One of the two supports (in yellow) for the footbridges between two pavilions at the Milan Fair.

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Tales of Life and Corrosion

Corrosion and Emotions

The corrosionist's profession offers true emotions

Those who study corrosion are often captivated by the beauty of the phenomenon. "Beauty," as Pasolini wrote, "can follow the strangest paths, even those not defined by common sense." Corrosion confirms this. I have always taken pleasure in preserving, when possible, the cases I've had the opportunity to work on, classifying them based on the morphology of the attack, the type of material, and the environment. I observe them under the microscope (opening up another marvelous world). With the specimens I have collected from various places over the years, I've created an archive that I pompously named the *Museum of Corrosion*. It is certainly the richest in Italy and is available to students. As with any respectable museum, some pieces are precious in that they relate to rare cases or objects from the past, while others document very common phenomena, but are equally important in providing completeness to the collection.

Sometimes, emotions are tied more to the significance of the work on which corrosion occurs than the phenomenon itself. Assessing the conservation status of a gilded Renaissance bronze or an Etruscan artifact or a sculpture that you've already had the chance to admire in art history books is certainly not the same thing as dealing with corrosion issues on a heat exchanger or a highway overpass. Even an orthopedic prosthesis removed from a patient involves more than a component

The Museum of Corrosion at the Politecnico di Milano @PolilaPP.

taken from a pump. Sadly, sometimes the emotion stems from the dramatic and even fatal consequences that corrosion, fortunately rarely, can cause, such as the collapse of a building, the rupture of a gas pipeline or a reactor, the breaking of a cable in a ski lift, or the crashing of a lamppost onto a busy street.

At other times, it is the adventurous journey undertaken to reach the workplace, or the workplace itself that can be exhilarating. I've found myself crawling through the hidden compartments of a ship, inside a steam generator, or in a crematorium. I've entered tanks so vast they could hold a football field; accessed restricted areas of famous landmarks, art galleries, or nuclear power plants; trekked across the desolate plains of Kazakhstan or sweltered under the equatorial sun; witnessed the sunrise or sunset amid desert dunes; experienced vertigo while atop the Sydney Opera House, the roof of San Siro stadium, and Milan Central Station; landed with a helicopter on an offshore platform, and from there, using special rubber boats, transferred to others, conquering the long Atlantic waves (and fear). One evening, in French Congo, Alberto and I were even arrested – another unique experience!

Finally, the actual work of a corrosion specialist, who diagnoses and combats degradation like a doctor, can be thrilling. While the patient cooperates in reconstructing the causes of their ailment, here the patient doesn't speak, so the corrosion specialist, at times, is transformed into an investigator. In these cases, solving a corrosion problem is like solving a little mystery.

You Never Forget Your First Consultation

Dany and I were newly appointed assistants at Politecnico di Milano: he in metallurgy, and I in physical chemistry. Our salaries were barely enough to make ends meet, so we quickly made a pact. If an opportunity for consultation arose, we would seize it together. If the consultation was predominantly electrochemical or related to corrosion, he would assist me, and I would do the same for him if it involved metallurgical issues.

After some time, we received a request for an opinion regarding a vague corrosion case from a nearby company in Brianza. We set off immediately. During the journey, Dany, evidently concerned about my inexperience, tried to brief me on how I should behave. He told me, "I recommend that if we quickly understand how to solve the problem, no one must notice". I'm not saying one should do as my former boss did, but we can learn something from him. When we went to the "siderurgical" plant in Taranto for the corrosion of heat exchangers and immediately understood the problem and the recommended solutions, he requested the equipment drawings and operation manuals, took photos of everything possible, collected water and metal samples, forced me to measure improbable corrosion potentials, and then, addressing the engineers who were anxiously waiting for an immediate answer, declared: "The case is interesting and complex. It deserves in-depth laboratory analyses and investigations. We will get back to you in two or three weeks." We brought everything back to Milan, and only after 20 days, he sent a report that, after an extensive but entirely useless introduction full of photos, graphs, and tables, stated in a few lines what we had understood from the very beginning. Along with the report, he sent an invoice commensurate with the "complexity of the case".

In the meantime, we had arrived, and Dany introduced me as a professor to the owner, who didn't seem overly impressed. He immediately took us inside the factory and showed us a large chromed cylinder within a machine used to produce, if I recall correctly, photographic film. He said, "You see, an emulsion is spread on the chromed surface of the cylinder. As it rotates, hot air jets evaporate the solvent and water, leaving only a cellulose film. This cylinder has corroded four times in the same way and at the same spot. After a couple of weeks, the right side loses its shine, and the film starts to become imperfect. After a month, craters even form, and the film is ruined. The cylinder must be disassembled and sent back to Germany for repair each time. This little problem costs me an arm and a leg, not to mention the downtime. You're not the first experts I've called. I've had someone from Bergamo come here, even with a pendulum, but he didn't give me the right advice." While we were ascending the system to closely examine the cylinder, I whispered to Dany, winking at him, "Maybe he also needed a good luck charm."

I was fortunate, or rather unfortunate, to understand the cause of the phenomenon immediately. To be truthful, two clues that had eluded my colleague with the pendulum helped me. I learned that the heater resistance in the blower, which blew hot air onto the corroded part of the cylinder, had burned out several times without any apparent reason. I also noticed that the blowing element was connected to the system that continuously applied the emulsion to the same part of the cylinder. Linking these two observations, it became immediately obvious to me that this system was drawing power from the poorly insulated heating element and discharging it to the ground through the emulsion and the cylinder, causing the attack on the chromed surface. At that time, I knew little about the problem of corrosion due to alternating current interference, so I had no doubts. Today, I would be much more cautious. In any case, I discussed my findings with Dany, and he agreed with my assessment, especially given the specific location of the attack and the extremely short time it took to occur. Suddenly, contrary to his instructions and under his shocked gaze, I reported my diagnosis to the owner and even provided him with instructions to resolve the issue. In less than an hour, we were already on our way back. Dany, furious, wouldn't speak to me.

We waited for two or three weeks, then called to inquire about the situation. The owner, pleased with the outcome, confirmed that the problem seemed to be resolved. We thought it appropriate to request 200,000 Italian lira, which we would then share. At that time, it was undoubtedly a significant sum. However, it didn't seem unreasonable because we had worked together, solved the case, and saved the company a considerable amount of money. So, we sent the invoice. The following month, instead of a check, we received a letter in which the gentleman from Brianza essentially stated that the work of two recent graduates, which lasted less than half an hour, was worth no more than 20,000 Italian lira. After a year of negotiations, we agreed to accept 40,000 Italian lira. Since then, in the few consultations we've done together, Dany has always wanted me to assist him and refer to him as "professor".

Truly Special Corrosion Products

In 1967, under the direction of Professor Roberto Piontelli, I was studying the corrosion rate of copper in solutions of copper sulfamate, which was exhibiting a significantly higher corrosion rate than expected. While investigating the cause of this anomaly, we found that, in the presence of sodium or potassium ions, white copper compounds formed on the copper surface in the shape of white needle-like crystals that did not deteriorate in the air. This was a rarity because copper salts, in general, are not stable. Chemical analysis and X-ray diffraction showed that these were two new compounds: copper and sodium double sulfamate and copper and potassium sulfamate, respectively. We found a way to produce them in large quantities and at low cost by stimulating corrosion with direct or alternating current. At this point, we thought of patenting a range of applications for these compounds. Among them was their use as a replacement for copper sulfate in the preparation of Bordeaux mixture (*a copper fungicide used in agriculture and gardening*). We said to ourself, "The anti-cryptogamic activity of copper sulfamate ions is certainly greater than that of copper sulfate ions. And if we use the potassium salt, once its primary action is completed, it could transform into a fertilizer." In other words, a brilliant idea, more than that, a guaranteed success. And finally, a case of constructive corrosion!

Since you can safely handle copper sulfamate, whereas handling sulfuric acid is not advisable, neither of us doubted that sulfamate ions might be significantly more aggressive toward plants than sulfuric ions. In any case, we sent some samples to the Institute of Plant Pathology at the University of Pavia for phytocompatibility testing, because of course, there should be an official certification when we move on to the commercial phase, which is to collect royalties.

In the meantime, to expedite the process, we decided to conduct tests ourselves. I prepared these salts, and we assigned ourselves tasks. The Professor was supposed to give them to his gardener and persuade him to spray them on the hydrangeas in his villa in Santa Margherita Ligure. I, more modestly, had to give them to my uncle

Antonio and ensure he try them on a row of grapevines and a field of potatoes in Mese, Valchiavenna.

We achieved our goal. Nut the following week, disaster struck. The new product destroyed the Professor's hydrangeas and my uncle's grapevines and potatoes in just a few days. It even burned the zucchinis in the garden because, to please his nephew or out of pride in participating in the prestigious research of the glorious Politecnico, my unsuspecting uncle decided to expand the experimentation, which we could indeed call "in the field."

After a month, the now useless verdict from the University of Pavia arrived. On official letterhead and bearing a stamp, the salts were officially declared lethal even for the hardiest shrubs. In other words, something akin to competing with the defoliants being used in Vietnam at that time.

The only ones who weren't surprised by the belated verdict were the gardener and my uncle, who had immediately realized that the "anti-cryptogamic" was actually a herbicide. Unfortunately, the idea that the Progress of Science might also require personal sacrifices never even crossed their minds. On the contrary, from the day of the incident, they bitterly resented it and didn't hide it. The gardener repeatedly made it clear to the Professor what he thought. Every time he met him, he added a sarcastic "Tou chi ü professü" to his greetings. My dear uncle didn't miss an opportunity to ask his nephew if his cutting-edge research at the Politecnico was always so interesting and useful. One day, when the naive nephew told him that the cultivation of potatoes was probably introduced to Valtellina and Valchiavenna, as had happened in nearby Como, by Alessandro Volta, he responded, "So it means that, back then, the electrochemists made potatoes sprout. Today, where they go, not even grass grows anymore." So the Professor and I, for a few months, confessed to each other with complicity what we had to endure over the weekends—him in Santa Margherita and me in Valtellina. And we joked about it. After all, it could have been worse. If, instead of an anti-cryptogamic substance, we had found something, let's say, anti-influenzal, we might have had the idea to make the gardener or my uncle try it. In fact, considering how badly they were behaving, maybe we whised we had found it! And we laughed. A bit reluctantly to be true.

Thank Allah!

In the late 1970s, I was contacted by a Milanese company that had designed a seawater filtration system for Amoco, the Arab oil company, to cool the condensers of a power plant. The system had recently been built in the Persian Gulf. Shell had supervised the project and construction on behalf of the client. The system consisted primarily of a huge stainless steel AISI 321 cylinder with a diameter of over 10 meters, rotating slowly around its axis, taking about an hour for each revolution. The cylinder was only partially immersed in water, so each point on its surface remained in contact with water for less than half an hour and longer with the atmosphere.

A few months after construction, the filter was already showing severe signs of corrosion.

The Milanese company, responsible for material selection, was held accountable for this, and they sought my collaboration to try and remedy the impending disaster. I believed that the only possible intervention was to apply a specific protection, known as cathodic passivation (sometimes called catanodic, often confused with anodic protection), to repassivate the stainless steel. This method is widely used today, particularly in offshore applications like protecting stainless steel pipelines in the North Sea. But at that time, there were only a few laboratory indications about this technique, and many doubted its effectiveness in the field, especially in the presence of cracks where corrosion was most evident. Moreover, the fact that the cylinder was only partially immersed and rotated slowly raised further questions about whether the protection would work, as it would only operate when the steel was immersed in water. Knowledge about secondary effects that extend protection for some time after the current flow is cut off was limited. So it was a new, untested type of protection and, moreover, intermittent.

I explained all of this to the Milanese company's management, emphasizing that I could not guarantee the success of this operation. I told them, "If this protection had been applied from the beginning, I would have no doubts about its effectiveness because it is much simpler to prevent corrosion than to stop it once it is initiated.

I'm sure it would work perfectly on a new system." I believed this was a valid point, but I understood that the prospect of installing a new system made them unhappy. To avoid this, they sent me to The Hague to meet with Shell's central office, along with the Italian representative for the contract, to present the intervention that I was beginning to regret proposing.

There, we met with Dutch and Arab technicians. I tried to convince them of the effectiveness of this protection, using Evans diagrams extensively. But I failed, perhaps because I was the first to have doubts. They said, "If you insist on proceeding this way, go ahead. We believe it is a waste of money, and in the end, you'll be the one to pay for it." The Milanese executives didn't give up and decided to implement the cathodic passivation, as they had no other way out. In a short time, a series of zinc anodes were installed on the cylinder's spokes, which was corroding more every day.

For several months, I received no updates and didn't dare ask, even though I was very anxious to know what was happening and, to be honest, worried. One afternoon, the director of the company supplying the anodes called me to say that two Arab engineers passing through Milan wanted to meet me to discuss a stainless steel filter. I immediately understood which filter they were referring to and rushed to meet them with much trepidation. I was led into an office where two of the technicians I had met in The Hague were waiting. They stood up, greeted me with big smiles and bows, and one of them said, "Praise Allah, who stopped the corrosion!" They both, speaking to me with great cordiality, added that the filter was now performing perfectly, even in the cracks. Trying not to reveal my happiness and acting as though I had never had any doubts, I said, "This is exactly what we expected."

That evening, on my way back home, I thanked Allah as well.

P.S. Recently, entirely by chance, I learned that several more of these filters were designed and built after the first one. All of them were made of stainless steel AISI 321, complete with zinc anodes. Nobody had told me. Evidently, I no longer needed to go to The Hague to convince the Arab clients and Shell inspectors of the effectiveness of the method.

A Good Old Embarrassment

During my early years of teaching the corrosion course, I engaged students in various practical exercises. Two of them were related to crevice corrosion. The first one aimed to make them observe the phenomenon. A stainless steel tube or plate (usually of AISI 304), around which a rubber band had been wrapped, was placed in a concentrated hydrochloric solution, and after just a few days, corrosion could be observed under the rubber band. The second exercise was intended to convey the message that even seemingly mild solutions, over extended periods and in the presence of crevices, could cause corrosion.

In the second experiment, the tube or plate, still wrapped with the same rubber band, was immersed in a diluted sodium chloride solution so that corrosion could occur before the end of the academic year. Indeed, after a few months, when the lessons were coming to a close, we would check if corrosive attack had actually taken place under the rubber band.

In the initial years, this experiment always went perfectly. In fact, on one occasion, a tube was literally cut in half. So, at the beginning of each course, I would describe the experiment to students with the naïve pride of an enthusiastic novice teacher who believed he was revealing a remarkable wonder. I confidently predicted the outcome. However, in one particular year, things did not go as expected. Despite nearly six months passing, the stainless steel under the rubber band remained perfectly shiny and untouched. I conducted all necessary checks on the type of material used, chloride concentration, solution pH, and rubber band adhesion to the metal, but I couldn’t understand why corrosion had not occurred.

Confronted with irrefutable results, some students pointed out that I had been, at the very least, imprudent in predicting the outcome because, evidently, corrosion phenomena were not as predictable as I had always shown. Others escalated this critique, asserting that the course I taught should be seen as a collection of empirical observations about material behavior rather than a true technical-scientific discipline. Another student, without mincing words, added, "How can you still talk about the science of corrosion and rational methods for prevention if you can't even predict the behavior of stainless steel wrapped in a rubber band?"

Caught off guard by this collective challenge and unable to provide a plausible explanation for the lack of corrosion, I had to admit that evidently, the phenomenon of corrosion was not entirely predictable in all its aspects. To get myself out of the situation, I paraphrased Professor Piontelli, a highly respected lecturer, to the students who were contesting me, and stammered, "Indeed, the field of corrosion, born from empiricism and still a devoted subject to it, may never be entirely emancipated from it."

It was a cop-out because Professor Piontelli, despite starting from the same premises, had always drawn opposite conclusions. I myself had thundered multiple times during the course that it was no longer tolerable for this field, with all its technical, economic, and social implications, to be dominated by practitioners and charlatans, whether they held positions or not.

In short, it was an embarrassment. It was only a year later, from some students working on their theses, that I learned about the prank they had played. To prevent corrosion from occurring, they took turns almost daily, throughout the experiment's duration, moving the rubber band around on the surface of the steel. At the end, they orchestrated the fake challenge.

In hindsight, I believe I can say that the experiment was not a failure. In fact, the students, evidently masters of the corrosion phenomenon, had figured out how to prevent it and had played along for six months. Probably, even today, some of them, working in various engineering fields, remember how to prevent crevice corrosion because they have not forgotten the prank they played on their naïve, novice teacher.

I have been re-implementing this experience in recent years, and every year, I hope that students attempt to deceive me again. Unfortunately, when we lift the rubber band in May, crevice corrosion invariably appears, strikingly evident and somewhat obscene.

Corrosion and Somalia

Starting in 1975, every other year I taught for five semesters at the University of Mogadishu. Especially during my first three semesters, I dealt with corrosion, traveling both to the north and south of the country. If memories of those trips are still alive, it is not just because of the corrosion phenomena I had the opportunity to witness. When they occur in tropical countries, especially along the coast, it seems like they challenge the corrosion scientist with their violent effects and, I would say, their unpleasant manner of display. Yet my memories of that time remain vivid mainly because of the extraordinary nature of those places.

Johar, tank for the concentration of sugar solutions.

Like the Village of the Duke of Abruzzi in Johar, where I had several discussions with the sugar factory technicians who regularly changed (within a few years, Italians were replaced by Cubans then Somalis) but their concern for corrosion and the difficulty of finding spare parts never changed. The residence of the Duke of Abruzzi was not far from the factory: a modest villa surrounded by bougainvillea, transformed into a small museum that housed not only the furnishings he used but also mementos from his explorations and personal items. A little further on, the neat white cemetery with his tomb. Next to it, the Uebi Scebeli River, with the hippos.

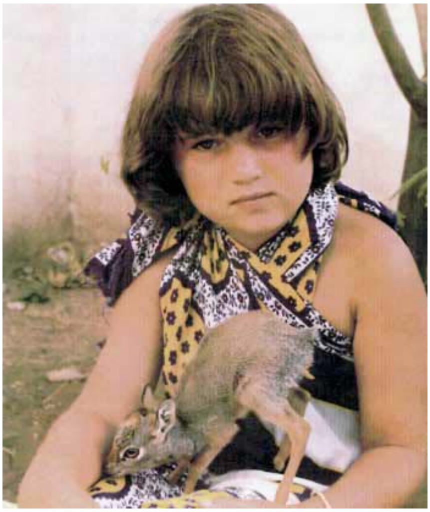
Or, like the southern part of Somalia, where I spent a week assessing the condition of a meat factory not far from the Juba River, abandoned by Russian technicians. Everything - structures, autoclaves, boilers, water treatment plant, rolls of tinplate still in the warehouse ready to be used - was corroded. I was there to understand the causes of perforating attacks on almost new equipment in a factory 60 kilometers further north, near the marker that indicates the equator. We would depart from Kismayo in the morning and return in the evening to spend the night there. Along the red dirt road, in the enchanting atmosphere of dawn and dusk, you could see gazelles, tall and majestic baobab trees, mysterious caravans of always-moving camels (and one evening, even a family of elephants).

Or, like the town of Brava, beautiful, with its Arab and Portuguese history. The first time I arrived there in ‘75 I was in a Russian military helicopter. The landing on the beach comically frightened the camels, which were standing under the palm trees with one of their front legs tied. In the same place two years later, I witnessed a scene that seemed like a Hemingway reference: an old man, with great effort, reached the shore on a tiny boat and then dragged an enormous blue marlin onto the sand. I have returned several times to this dreamlike beach, which is also a monument to marine corrosion. In the sea, there were the remnants of a steel pier built by the Italians in the 1930s; in the area exposed.by low tide there was a small cannon from World War II with its steel parts nearly gone, and the skeleton of a ship, probably wrecked after crashing into the coral reef; not far away, electrical equipment in copper, aluminum, and steel abandoned by the military, infested with galvanic corrosion; at the edge of the beach, a building from the 1920s or ‘30s, resembling something from One Thousand and One Nights, completely destroyed in all its reinforced concrete parts. The comparison with the reasonably preserved old stone houses a few meters away was more instructive than any lesson on the durability of structures in a marine environment.

Or, like in Merca, where from the house of our friends Licia and Giulio overlooking the Indian Ocean, we would gaze at the stars in the evening. In the port, still rusty, there were the rings to which, not many decades before, they used to tie slaves before boarding them. Or like in Adale where, on the dune facing the Indian Ocean, the University had established a wind speed monitoring station and built an experimental windmill that was used to pump enough water from a well for the entire village until corrosion made it unusable. To reach it, you would cross the gazelle plain, the area of mirages, War Shek, and then continue through the bush along an endless track constantly crossed by dick-dicks. Or again, like in Gesira, with the sand dunes that made even the rusty refinery and the fertilizer production plant - which never went into operation - look beautiful. Or like in Baidoa or Burakaba, far from the sea, where the corrosion rate couldn't even be measured, the atmosphere being so unpolluted and the climate so dry.

In developing countries, it is often observed that near companies you can find machinery or equipment that is out of order, water tanks with a perforated bottom, old tractors or trucks in a state of disrepair. They are covered by a layer of rust that takes on reddish tones when it is porous and thick, while it becomes dark brown when it is adherent and compact, as often happens with cast iron. It can also happen that some areas still have the white-gray color of zinc or retain some red traces of red lead or green due to the presence of copper parts. In Somalia as well, where it is not convenient to recover discarded equipment or machinery you can see around rusty monuments of agricultural or industrial archeology harmonize with the landscape. Of course, the corrosion expert usually looks at these relics with curiosity and professional distortion. He observes the extent and morphology of the corrosion, the behavior of welds or riveted areas, the distribution and morphology of the corrosion products, often of captivating beauty, and provides technical judgments, albeit belated and unsolicited, on the choice of materials or construction details. Yet, in some cases, emotions prevail in him.

About a hundred kilometers north of Mogadishu, on the way to Belet Weyne, in an uninhabited area not far from the remains of a petrified forest, there's a very old steam tractor complete with steel wheels and a chimney that makes it look like an old locomotive.



MariaPia Pedeferri accompanied her father on study and work trips to Somalia: in the photo, she is seen petting a small antelope.

The passage of time has covered it with a layer of rust that is uniform and attractive, almost like a finish. It is thrilling to see it suddenly appear in front of you, but even more so to learn that in that area, just after World War I, several Venetian settler families had worked to establish a farming enterprise, and that, after a few years, struck by malaria and hardships, they had to give up. The vegetation has erased all traces of that endeavor. Only the tractor remains to bear witness to it.

Brava, remnants of a ship on the beach

Somalia, old steam tractor on the way to Belet Weyne

Much further south, there is another wreckage that recalls an even more dramatic and ancient adventure. I haven't seen it in person; a colleague told me about it. In 1864, a German expedition led by Claus von der Decker set out with two state-of-the-art steamboats with flat steel bottoms to navigate the Jubba River, with the intention of penetrating as far inland as possible, then continuing on foot to Ethiopia. One of the boats sank right at the river's mouth, while the other, after collecting the survivors, sailed up the river for more than a hundred kilometers. However, it ran aground shortly after Bardera and was attacked by a band of guerrillas, resulting in the massacre of all the explorers. The boat remained stranded in a bend of the river that silted up over the years. The hull, completely corroded, disappeared, but in the midst of the vegetation, one could still see, or rather used to see, the rusted smokestack. Inside it, a plant had grown.

Imagination: A Necessary Quality for a Researcher

During my stay at the University of Connecticut in 1978, Professor N.D. Green hosted Professor M. Stern who just over twenty years earlier, together with his collaborator Geary, had introduced the law known as the Stern-Geary law and the method of linear polarization that allows for a simple and elegant measurement of corrosion rate. At that time, Stern was no longer working in academia; he had left teaching and research to take a leadership position in a large multinational corporation. During lunch, Stern shared the story of how the law that made him famous had originated. The next day, Green roughly conveyed to me what I am reporting here.

In the mid-1950s, some of Stern's students obtained a scholarship for a one-year study stay in Germany at the laboratories of a well-known electrochemist of the time, K.F. Bonhoeffer, to study the corrosion behavior of metals. Once in Europe, the students began their work by obtaining the necessary equipment and reagents. However, after a few weeks, they embarked on an extensive sightseeing tour of England, France, and Italy. Returning to the laboratories only a couple of months before the end of the scholarship, they realized they no longer had the necessary time to complete the program they were supposed to carry out, which involved weight loss measurements for different metals in different environments. Undeterred, they decided to invent these measurements, which were long and tedious. More precisely, to give them a semblance of coherence, they thought of deriving them from electrochemical measurements that could be done quickly. Immersing the samples to be studied in various solutions, they applied a predetermined anodic current and recorded the potential variations. They then assigned corrosion rates values inversely proportional to the measured polarizations and reported these data in the final report, alongside the results of electrochemical measurements, passing them off as "corrosion rates determined by weight loss measurements."

Back in the United States, the students submitted the report. Stern, who did not overlook the connection between polarization and corrosion rate, could not imagine that the students had invented it. He sensed its great importance and, assisted by his collaborator Geary, replicated the measurements on other materials and environments. To the surprise and relief of those who had fabricated the data, he confirmed the relationship between polarizability and corrosion rate and also theoretically derived what would later be called the law of linear polarization or Stern-Geary law. He then published everything in an issue of the Electrochemical Society in 1957.

Meanwhile, in Stern's laboratory, the electrochemical measurements made in Germany were repeated, and it was found that many of them were incorrect. In addition to the weight losses, the students had also invented many of these measurements. They were forced to confess but, perhaps due to the results and honors that Stern had meanwhile obtained, partly thanks to their deception: they were not punished. After all, they had made a significant contribution to the discovery of the law of linear polarization. This is what I seem to remember from Green's speech. But perhaps I have also invented something.

Crows, Owls, and Talking Crickets

There is a type of consulting work that I have always done reluctantly, avoiding it, if possible. That is serving as an expert witness in legal cases, arbitrations, or commissions where the issue at hand concerns who should be held responsible for damages caused by corrosive phenomena and to what extent. The atmosphere is usually contentious: even calm and pacifist individuals in those settings can turn into intolerant beings. Their mission is not the pursuit of truth but the victory of their clients, and the two things often do not align.

Often, the experts in such cases are well-balanced and knowledgeable about corrosion, but sometimes they know nothing about it. In such cases, the worst happens when one of them wants to exonerate their represented party and resorts to making extravagant claims. The more outrageous the claim, the more confidence they seem to have in making it. I once heard a so-called corrosion expert tell me, "Perhaps you've never heard of cathodic protection?" as he argued that atmospheric corrosion could have been prevented using this technique. On another occasion, a colleague insisted that the issue under discussion was certainly a case of galvanic corrosion because the electrolyte between the two isolated metals happened to be particularly conductive. When they have nothing else, they fall back on the weapon of stray currents. Some experts seem to see them everywhere, and if you attempt to express a different opinion, they imply that only a select few technicians, including themselves, are truly experts in this field.

Things don't always go well, even when a serious corrosion expert tries to persuade the technician appointed by the judge or the judge themselves about things that seem obvious to those who understand the subject. For example, that small variations in the structure of the metal or the composition of the environment can render conditions of passivity labile or susceptible to corrosion attacks, or that water is not always the pure and precious "sister water" of Saint Francis, but that when it stagnates in the sheaths of pre-stressed concrete structures or inside equipment after a hydraulic test, it can become the most perfidious stepmother. I'm not making these examples up; these are real cases that have been the subject of endless discussions during judicial expert testimonies in which I have participated.

In these meetings, a surreal atmosphere often arises, much like the one Collodi described when the Blue Fairy, after having Pinocchio removed from the oak tree to which he was hanged, summons the most famous doctors in the neighborhood, namely: the Crow, the Owl, and the Talking Cricket, to determine whether the puppet is alive or dead. "The Crow, advancing first, felt Pinocchio's pulse: then he felt his nose, then the little toe of his foot, and when he had thoroughly examined him, he solemnly pronounced these words: "To my thinking the puppet is beautifully dead, but if, unfortunately, he was not dead, then that would be a sure sign that he is still alive! I am sorry, said the Owl, to have to contradict my illustrious friend and colleague the Crow: to me, on the contrary, the puppet is always alive, but if, unfortunately, he was not alive, then that would be a sign that he is really dead. And what do you say?" the Fairy asked the Talking Cricket. "I say that the prudent doctor, when he doesn't know what he's talking about, the best thing he can do is to remain silent." In legal cases, I have often encountered Crows and Owls, but rarely Talking Crickets.

Writers and Paintings

Two prominent Italian writers have had connections with the world of protective coatings: Italo Svevo and Primo Levi. Svevo, at the beginning of the last century, served as the commercial director of *Società Veneziani* in Trieste (owned by his father-in-law), which was a leader in the field of submarine protective coatings. During those years, Trieste was part of the Austro-Hungarian Empire, and *Veneziani* was known as a supplier to the Austro-Hungarian Navy, providing a special anti-fouling paint for protecting warship hulls, which was named *Moravia.* After 1918, when Trieste became part of Italy, the same product was supplied to the Italian Navy. To be able to negotiate with the British Admiralty, Svevo even took English lessons from none other than James Joyce, who was teaching in Trieste at the time. The author of "Ulysses" became friends with Svevo and assisted him in publishing his works, and he was briefly an employee of *Veneziani* as well. Primo Levi, who mentioned these details in the appendix of his "*The Periodic Table*" (*Il sistema periodico* published by Einaudi in 1975), notes about the *Moravia* paint: "The coincidence with the pseudonym of the famous Italian writer is not accidental: both the Trieste industrialist and the Roman writer derived this name from a common relative on their mother's side.

Primo Levi, the author of "*If This Is a Man*," after his harrowing experience in Nazi extermination camps, worked for many years in a paint factory, first as a laboratory chemist and later as a manager. Several references to his profession can be found in his works. We'd like to provide two quotes from "*The Periodic Table*".

The first one helps to understand the complications that the paint solidification process can present. "Paint is an unstable substance by definition: in fact, at a certain point in its career, it must change from a liquid to a solid state. This must happen at the right time in the right place. The opposite case can be unpleasant and dramatic: a paint may solidify (we crudely say it *"fails to dry"*) while in storage, and then the goods must be discarded; or the base resin may solidify during synthesis in a reactor of ten or twenty tons, which can turn into a tragedy; or, on the contrary, the paint may not solidify at all, not even after application, and then people laugh at you because a paint that doesn't *dry* is like a gun that doesn't fire or a bull that doesn't impregnate."

The second one allows for a commentary. "That of painters is an ancient and, therefore, noble art: its most remote testimony is in Genesis 6:14, where it is narrated how, according to a specific specification of the Almighty, Noah covered (probably with a brush) the inside and outside of the Ark with molten pitch. But it is also a subtly fraudulent art, like that which aims to conceal the substrate by giving it the color and appearance of what it is not: in this respect it is related to cosmetics and adornment, which are equally ambiguous arts and almost as ancient (Isaiah 3:16 and following)." The art of applying protective coatings can also be subtly fraudulent in some cases. This happens when the choice of materials, the protection process, the surface preparation, or the method of applying the paint are not done correctly. As a result, the coating obtained covers the underlying metal surface but does not provide the required protection for the expected service life.

Lead Corrosion and the Fall of the Roman Empire

A daily ingestion of just a few tens of micrograms of lead can cause progressive poisoning with very serious consequences. From initial headaches and loss of appetite, it can lead to anemia, abdominal colic, male and female sterility, blindness, mental and epileptic disorders, and even madness. Lead poisoning, as this type of poisoning is called, was also a recognized occupational disease in the past, leading to casualties among workers in the industries of lead extraction, refining, and processing. There were casualties among typesetters when printing still used lead typefaces, among workers in the battery industry, and among painters who used red lead or white lead daily (hence the saying *crazy as a painter*). Some historians have cited lead poisoning among the causes of the fall of the Roman Empire, while others contest this hypothesis. In this context, we will explore how, according to historians in the first group, the Roman aristocracy might have been exposed to lead, drawing primarily from the work *Lead Poisoning and the Fall of Rome* by S.G. Gilfillan (Journal of Occupational Medicine, 7, 2, 1965). Obviously, the Romans didn't have an understanding that lead could lead to poisoning. However, as early as the 2nd century BCE, lead poisoning (saturnism) had been identified as an occupational disease among those involved in the mining and processing of this metal. During the Augustan era, Vitruvius in particular had warned about potential health risks associated with lead ingested through water. In his work *De Architectura* (8.6.10), he wrote: "Water conducted through earthen pipes is more wholesome than that through lead pipes since it is found that water becomes deterious in lead pipes because it dissolves the lead. Therefore, if we want to safeguard our health, it is preferale to avoid the transport of (our) water through lead pipes."

Let's return to the Romans. They ingested lead in their water, beverages, especially wine, and in their food which was contaminated by lead containers or utensils used in its storage and preparation.

Let's look at the water. If the water brought into Roman homes through lead pipes was hard and alkaline, the amount of dissolved lead was negligible. In fact, the replacement of lead pipes in some European cities with hard and alkaline water has occurred only in recent decades. However, when the water had low hardness and a low pH, such as rainwater, which has both characteristics, the amount of dissolved lead was not negligible, especially if the water had been collected and stored in lead tanks.

Moving on to wine, the major source of ingested lead for the Romans was wine and its derivatives, which were consumed almost exclusively by the aristocratic class. This explains why only the wealthy were affected by lead poisoning. Gilfillan lists 14 ways in which lead could enter wine. We'll mention just two. Wine, especially if acidic, could corrode the lead used in the containers in which it was stored, such as amphorae. A greater quantity of lead could enter the wine through a grape syrup that was often added. This syrup was rich in lead because it was obtained by concentrating grape juice before fermentation in pots that were lined with lead. The presence of Saturnine metal in wine was appreciated because it gave it a sweet taste and increased its shelf life. In fact, those who could afford to drink wine at lunch and dinner consumed a daily dose of lead that was certainly higher than the 45 μg recommended by the World Health Organization as the limit not to be exceeded.
The aforementioned syrup was not only used as an addition to wine but also for preserving olives, various types of fruits, and in food preparation. Luxury dishes that used this syrup are described in the works of Apicius, who could be considered the "Artusi" of his time.

Studies on bones found in Roman tombs confirm the presence of lead in individuals from the dominant class. Furthermore, historians tell us down that many members of this class, including emperors, exhibited typical symptoms of lead poisoning. For example, Claudius, who was known for his affinity for wine, suffered from speech impediments, joint problems, frequent, prolonged, and unjustified bouts of laughter, recurring stomachaches, and mental disorders that drove him to the brink of suicide on multiple occasions. Likewise, Tiberius, Caligula, Nero, Galba, and Nerva, as well as most emperors of the late empire known for heavy wine consumption, exhibited some of these symptoms.

The Noble Patina

The term "noble patina" is reserved for the green patina formed by the corrosion of copper or bronze. Some of the earliest observations and reflections on the corrosive phenomenon concern this patina. Plutarch, in his work *De Pythiae Oraculis*, mentions a statue placed at the entrance to the sanctuary of Apollo in Delphi, which, despite being centuries old, is covered with a patina of a brilliant, uniform color. He wonders whether this patina was created by ancient master sculptors using special mixtures or techniques, or if it formed due to the action of the atmosphere penetrating the bronze and pushing the corrosion outward. Another possibility he considers is that the bronze itself, as it aged, produced the patina.

In the Greek and Roman world, especially for bronze works, the preference was for a finish that showcased the natural color of the metal. The usual concern was to avoid rust formation (*aerugo*, bronze rust) through periodic cleaning and oiling. However, at times, artists would break with tradition and intentionally seek a corrosive effect rather than preventing it. For instance, on the horses of San Marco, artists carved into the gilding of the mane to tone down the brightness of gold with the color of the underlying bronze, or more precisely, its corrosion products. In some cases, artists not only used the corrosive process to finish a work that was essentially complete but also to express emotions and states of mind. Pliny the Elder tells of the sculptor Aristonides, who, in portraying Atamante distressed for having thrown his son Learco from a cliff, used a copper and iron alloy so that the iron, rusting within the shiny metal surface, could convey the man's shame and dismay.

During the Renaissance, the art of bronze casting experienced a resurgence, and artificial patination was born. Vasari wrote in his treatise on sculpture: "Bronze naturally darkens over time, turning black rather than red, as it appears when worked. Some turn it black with oil, others make it green with vinegar, and yet others give it a black color with varnish, each according to his taste." The widespread use of artificial patination took place in the first half of the last century. Even though various treatments and recipes were employed, resulting in different colors, patination remained an art based on the skill and creativity of those who executed it, rather than just technical knowledge. In fact, it was often the artists themselves who applied patination.

Even later, it didn't become a process that could consistently yield completely predictable and reproducible results. Notably, a sculptor like Henry Moore, in 1967, referred to it as an exciting but unpredictable process. He wrote, "Bronze, when exposed to open air, especially near the sea, naturally develops a beautiful green patina over time. However, sometimes we cannot wait for nature to take its course, so we try to speed things up by treating the bronze with various acids that produce different effects. Some make the surface black, others red. Usually, when I prepare a casting, I have an idea of the bronze finish I want, whether dark or light, and the color I intend to achieve. When the cast comes back from the foundry, I apply the patina, and sometimes it turns out well, but sometimes you can't replicate what you've done on other occasions. The patination of bronze is an exciting process, but it is not very reproducible." (H. Moore, Henry Moore on Sculpture, 140, Philip James, New York, 1967).

The Art of Corrosion

Leopoldo Nobili and Metallochromic Art

Leopoldo Nobili, a nearly forgotten scientist of the early nineteenth century who made significant contributions to the fields of electromagnetism, thermoelectricity, and electrochemistry, was the first to explore metal coloring through anodic oxidation for both scientific purposes and to assist the arts. His research in this field began in Reggio Emilia in 1826 but was abruptly interrupted in 1831 when, after the uprising in his city against the Estense Duke and the subsequent restoration imposed by Austrian troops, he had to leave Reggio and seek refuge in Paris. The following year, with the intervention of a group of friends in Florence, Grand Duke Leopold II called him to Florence and, despite his past as a liberal and republican, appointed him as a professor at the Imperial Regio Museo of Physics and Natural History. This allowed him to fully resume his research activity in the museum's laboratory.

Unfortunately, only three years passed before an old ailment he had contracted during the Russian campaign - as artillery captain with Napoleon - resurfaced. He suffered greatly during the disastrous retreat and especially in his brief but dramatic captivity. He died prematurely on August 17, 1835. He was buried in Santa Croce, where his tomb bears the inscription: "To Leopoldo Nobili [...] with high theory and admired discoveries in the science of physics, promoter of metallochromy, inventor, and master of this art."

LEOPOLDO NOBILI

Trassilico - July 5, 1784
Florence - August 22, 1835

Father of the metallochromic art.

Nobili writes in 1830: "In 1826, I discovered a new class of phenomena which I named electrochemical appearances. One of the main experiments consists of placing a platinum point above a sheet of the same metal. The point is positioned vertically over the sheet, which is in a horizontal position at the bottom of a glass or porcelain vessel. A solution of lead acetate is poured into this container. The point is then connected to the negative pole of a battery, and the sheet is connected to the positive pole. At the very moment when the circuit is completed, a series of colored rings similar to those that appear in the middle of Newton's lenses, forms on the sheet, precisely below the point. This phenomenon, which surprises anyone who observes it for the first time, led me to the discovery of several others."

At this point, it may be appropriate to interrupt Nobili's account to provide some additional information. The passage of current between two metal electrodes immersed in a lead acetate solution produces a lead dioxide film at the surface of the positive electrode, which functions as the anode. This film gives rise to the interference phenomenon, resulting in the appearance of different colors on the surface depending on the film's thickness. Therefore, if the geometry of the system used – that is, the anode, cathode, and cell – is such that the current is uniformly distributed on the anodic surface, a film of uniform thickness and color is obtained. If this is not the case, the thickness varies on every part of the surface and changes with the local current density. Consequently, the colors also vary, creating a chromatic mapping of thickness and current density: the electrochemical appearances.

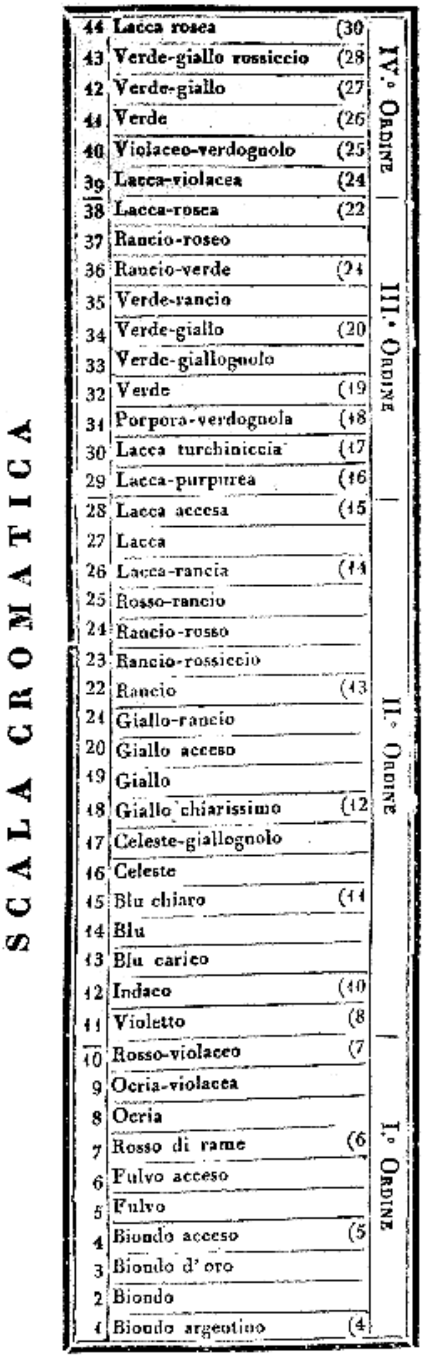
Let's return to Nobili's account. "I foresaw from the very beginning the benefits that the arts could derive from this new method of coloring metals, but it was only towards the end of 1827 that I started to seriously focus on this application. I will briefly mention the initial attempts and then pause to reflect on the products I obtained in the course of 1828, which I presented to the Institute of France in November of the same year. These consisted of many colored sheets that, due to the beauty of the shades, the precision of the contours, and the softness of the nuances, attracted the attention of the entire illustrious assembly. The art had reached the point of taking its place among the others: it needed a name to distinguish it. The name *metallocromia* was chosen upon the advice of the learned members of the Institute." (Francesco Bordè, Nobili's nephew, wrote a few years later: "And the learned members of that illustrious assembly were pleasantly surprised and pleasantly amazed that such charm and delicate harmony of colors could originate from the electric, which in lightning shines with such terrible light.").

The chromatic scale by Nobili

Nobili creates a total of 44 distinct shades on as many metal plates and arranges them in the chromatic scale shown in the figure ("the harpsichord of colors" in his imaginative language).

"[In the chromatic scale] the shades are arranged according to the order of the veils or thin plates from which they originate. The color of the thinnest veil is No. 1, and then the colors produced by the thicker veils follow. Therefore, these colors are produced by veils or thin plates, [just like] the colors of soap bubbles and the rings observed by Newton around the point of contact of two slightly convex glasses or lenses. The order of the colors should exactly match that of my scale, and it does indeed match."

Thus, he defines his tints of the first, second, third, and fourth orders based on whether they correspond to the first, second, third, or fourth Newton ring. He goes further by using tables from the English scientist to define the thickness of the oxide layer that produces different colors, assuming "that the refraction of the electro-chemical veils is the same as that of water," and he includes them in the scale alongside the various tints. He uses a unit of measurement as the millionth of an English inch, which is approximately 25 nanometers, and specifies: "So our scale would start with a veil of the same thickness as four of these units (about 100 nm) and end with one of the same thickness as thirty of the same units (about 750 nm)."



SCALA CROMATICA

44	Lacca rosea	(30	IV.° Ordine
43	Verde-giallo rossiccio	(28	
42	Verde-giallo	(27	
41	Verde	(26	
40	Violaceo-verdognolo	(25	
39	Lacca-violacea	(24	
38	Lacca-rosea	(22	III.° Ordine
37	Rancio-roseo		
36	Rancio-verde	(21	
35	Verde-rancio		
34	Verde-giallo	(20	
33	Verde-giallognolo		
32	Verde	(19	
31	Porpora-verdognola	(18	
30	Lacca turchiniccia	(17	
29	Lacca-purpurea	(16	
28	Lacca accesa	(15	II.° Ordine
27	Lacca		
26	Lacca-rancia	(14	
25	Rosso-rancio		
24	Rancio-rosso		
23	Rancio-rossiccio		
22	Rancio	(13	
21	Giallo-rancio		
20	Giallo acceso		
19	Giallo		
18	Giallo chiarissimo	(12	
17	Celeste-giallognolo		
16	Celeste		
15	Blu chiaro	(11	
14	Blu		
13	Blu carico		
12	Indaco	(10	
11	Violetto	(8	
10	Rosso-violaceo	(7	I.° Ordine
9	Ocria-violacea		
8	Ocria		
7	Rosso di rame	(6	
6	Fulvo acceso		
5	Fulvo		
4	Biondo acceso	(5	
3	Biondo d'oro		
2	Biondo		
1	Biondo argentino	(4	

"The small numbers in parentheses are taken from Newton's table, disregarding the fractions, and represent the values corresponding to thin water layers." The unit of measurement is the millionth of an English inch.

Nobili's chromatic scale is described in L. Nobili's *Mémoire sur le couleur en général et en particulier sur une nouvelle échelle chromatique déduite de la métallochromie à l'usage des sciences et des arts*, published in Bibl. Univ., 49, pp. 337 and 50, pp. 35, Geneva, 1830. An Italian version of this work was published in "Antologia," Florence, 39, 117, 1830.

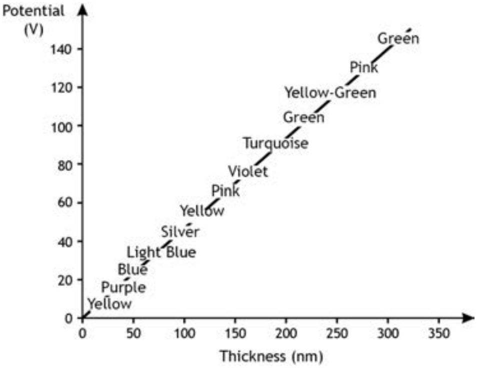
Nobili's work on nanofilms and his thickness measurements date back to before 1830, but unfortunately, he is not widely recognized for these contributions today.

Nobili's appearances have a place in the history of electrochemistry because they initiated studies on current distribution in galvanic systems and provided material for contemplation to numerous mathematicians and electrochemists who came after him. Eminent figures such as Marianini, Becquerel, De La Rive, Riemann, Mach, and Volterra were interested in solving field problems, like the electric field, governed by Laplace's equation. The appearances, in fact, represent a graphical or, more accurately, chromatic solution to Laplace's equation.

However, Nobili's *metallocromia* never gained the prominence among the arts that its inventor had hoped for.

Creative Oxidation on Titanium

Only two metals are inherently colored: gold and copper. All the others, around sixty, have shades ranging from gray to white. However, often their surfaces appear colored. Sometimes this happens because they are covered with patinas of corrosion products; other times because they are coated with an extremely thin and transparent oxide film, capable of reflecting and refracting light, thereby producing the phenomenon known as *interference*. That's what happens with oxidized titanium. In fact, if a film of oxide is produced on the surface of this metal, for example by passing a direct current from titanium to a counter electrode through appropriate solutions (anodically oxidizing the metal), the surface takes on colors that depend on the thickness of this film, which, in turn, depends on the applied potential. More precisely, by increasing this potential from a few volts to 140 V, the thickness goes from a few nanometers, i.e., a few millionths of a millimeter, to over 300 nm, and the colors change according to the sequence: yellow – purple – blue – azure – silver – yellow – pink – violet – turquoise – green – yellowish green – pink – green, with an infinite variety of intermediate shades. These colors are just as beautiful as those found in flowers, animals, minerals, or natural phenomena like rainbows, auroras, or sunsets.



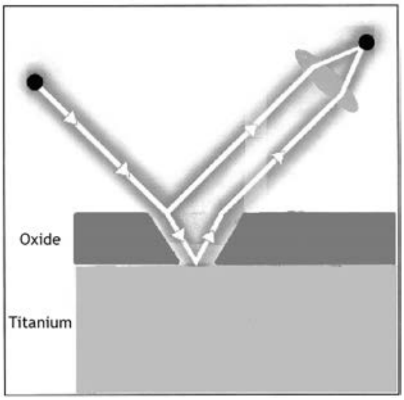
Relationship between applied potential and film thickness.

Potentials, oxide film thicknesses, and colors for the first scale on titanium

Interference colors can be obtained not only by anodic oxidation, although this remains the primary method to achieve them. Films of this type can also be obtained at high temperatures through reactions with oxygen, and not just on titanium but on many other metals. Interference colors, for example, can often be seen near welds, on the surface of chips produced by turning, on pieces subjected to heat treatments. And if we leave the realm of metals, interference colors are also seen in iridescent oil films on water, soap bubbles, feathers of certain birds (like peacocks), wings of certain butterflies, and the bodies of some fish and insects.

Interference phenomenon

When we observe a titanium surface covered with an oxide film, two overlapping light waves reach our eye: one reflected from the upper face of the film in contact with the atmosphere and the other from the lower face in contact with the metal. The second light wave, compared to the first, undergoes a double crossing of the oxide layer. If we assume that the titanium surface is illuminated with monochromatic light, this wave will be in phase with the other only if this additional path contains a whole number of wavelengths; otherwise, it will be out of phase or even in opposite phase. When the two oscillations are perfectly synchronized, they reinforce each other when superimposed. When the two oscillations are in opposite phase, they cancel each other out when added together. In intermediate situations, depending on the circumstances, we may have either additive or subtractive interference, leading to either reinforcement or weakening of certain color bands. Consequently, if we illuminate the titanium surface with white light, which, as known, contains all colors, the two waves for a specific color, i.e., for a certain wavelength, reach our eye in phase, resulting in reinforcement. For another color, the waves are out of phase, leading to extinction. For all other colors, there will be either reinforcement or weakening, depending on the situation. Naturally, as the thickness of the film changes, the colors that are reinforced, weakened, or even canceled vary, and therefore the hue perceived by the observer changes.

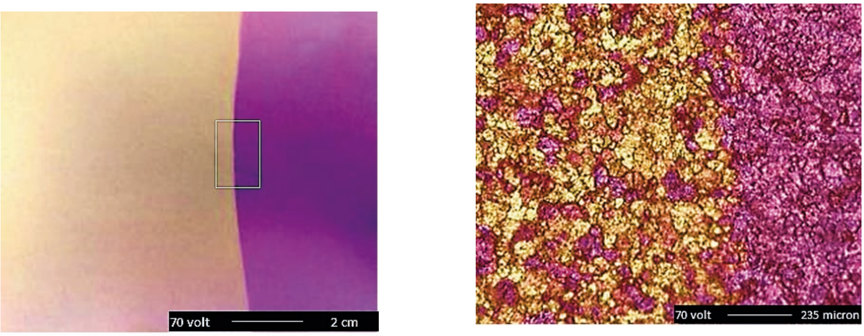


Interference phenomenon on the surface of oxidized titanium

Memory of Titanium

To achieve intense and precious colors, things are a bit more complex than outlined above. To clarify, it is necessary to recall a particularly unusual behavior of this metal. It's a behavior that seems to almost connect more to the living world than the inorganic world and can be seen as a kind of *imprinting*. As the behaviour of Lorenz's newborn gosling is influenced for life by the first moving object they see, so the value of the potential that titanium encounters in the first moments of its oxidation conditions the properties of the ensuing oxide with which it will be covered. This imprinting is early, in the sense that the behavior code that the potential communicates to the metal can only be registered in the very first instants of oxide growth, even though its effects become apparent once the growth is complete. This process is irreversible because it cannot be changed once established. Therefore, three situations can arise depending on whether, in the initial instants (i.e., the first thousandths of a second), oxidation occurs at potentials equal to, greater than, or less than a critical value that depends on the environment in which the process is carried out. If oxidation begins precisely at the critical potential, it results in a film whose thickness increases with the potential, exceeding 300 nanometers and displaying the entire range of colors previously described. Viewed under a microscope, these colors are perfectly uniform and distributed over the entire surface. This scale contains the richest variety of shades and displays the most intense tones and is referred to as the primary or first scale. X-ray diffraction spectra and Raman spectra confirm that the oxide films on this scale have an amorphous structure similar to glass.

If oxidation starts at values lower than the critical potential, only some faces of the crystalline grains that make up the metal are covered by the same amorphous film. On the other faces, a white film with an ill-defined structure forms instead. Therefore, you still obtain the primary chromatic scale but it appears more faded compared to the previous case, with the degree of fading increasing the further the initial potential deviates from the critical value. Lastly, if oxidation starts at potentials higher than the critical potential, crystalline oxides form, resulting in the colors of the secondary chromatic scale. This scale is less distinct than the first one, with colors ranging from reddish to turquoise to white, eventually taking on a brownish hue beyond 100 volts. After the initial moment, it is indeed possible to change colors, but only within the primary or secondary scale. You cannot transition from colors in one scale to colors in the other scale. At first glance, this behavior might seem limiting, like a piano that only activates the white keys or only the black keys depending on whether the first note is played on a white key or a black key. However, it's not a limitation but rather a characteristic that offers various applications based on what titanium's imprinting allows or restricts.



Titanium anodized with colors from the first (on the right) and the second scale (on the left) at both macroscopic and microscopic levels.

The Museum of Corrosion @PoliLaPP

Decorative applications

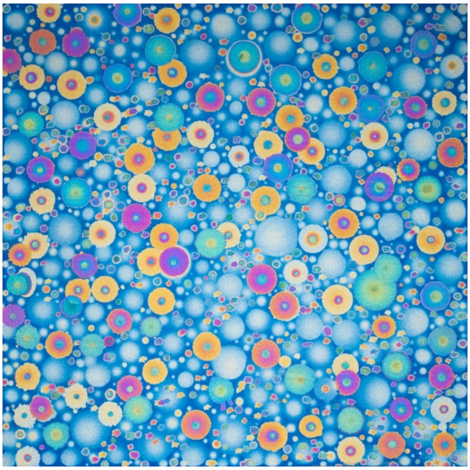
The availability of colors from the first and second scales in a wide range of shades, the ability to achieve surfaces with perfectly uniform colors or continuous gradients, or conversely, the option to localize colors on the titanium surface using appropriate masks, opens up the world of design and jewelry to titanium. The possibility of using a brush soaked in a saline solution and adapted to carry an electric current allows anodizing titanium to become a painting technique that could be considered traditional, or nearly so.

Appearances

Titanium allows us to obtain images of different origins that can be appropriately referred to as *appearances*. This term was introduced by in the early days of electrochemistry, Leopoldo Nobili the inventor of *metallocromia*. These appearances reveal invisible aspects of certain phenomena that have already occurred or are happening on the surface of titanium. We have categorized the first type as *field appearances* and the second as *motion appearances*.

Field appearances are achieved by oxidizing titanium with non-uniformly distributed currents. They represent a map of the thickness of the oxides produced or the charge exchanged. Under particular conditions and with some approximation, they also provide information about the current distribution on the titanium surface and the electric field in its immediate vicinity. In these cases, they represent the chromatic solution of Laplace's equation related to the electric field that generated them. These appearances thus photograph the nanostructured landscape of the oxides, and the various colors, like contour lines, depict its topography. They can naturally be varied in shape and color by changing the current distribution, operating conditions, or boundary conditions. They consistently present still, ethereal, stupefying landscapes. Even though they describe the infinitely small and complex world where nanotechnologies operate, they convey astral visions and sensations of levity, suspension, and a calm enchantment, as Calvino would put it.

The other appearances, those in motion, are obtained by applying oscillating



Balls (Tribute to Leonardo da Vinci)
1996
40 x 40 cm

potentials to titanium while it is immersed or comes into contact with a solution. Every time the potential deviates from the critical threshold or returns to it, changing the chromatic scale, the position of the liquid remains imprinted on the titanium surface. If the liquid is at rest, horizontal lines with spacings are produced depending on the frequency of the pulses and the immersion speed. However, if it is in motion, appearances emerge that combine the magic of titanium colors with the charm of the motion of wavefronts in the initial passing of free surface wetting the metal. Camilla Cederna, who saw some of these appearances in a preview in 1969, wrote in her weekly column on l'Espresso: "A fantastic mix of designs and colors, violet that blends with the entire range of blues, from the palest sky blue to the deepest cobalt, green that surrounds the purple and gold to fade into vague waves of blue; it's all a tangle of signs and lines that form a jungle, a maelstrom of symmetrical, watchful leaves, asymmetrical circles, and wavy lines, angles and lines in a hallucinatory chase, all an elegant hieroglyphic, often somewhat Art Nouveau."

These appearances depend on the modes of motion that generate them. Thus, they can be varied by bending and perforating the titanium sheets to be treated; by placing fabrics or nets or other obstacles on their surface; by changing the immersion methods, or agitating the solution to create waves, wakes, vortices, or rippling the

Japanese waves
1982
13 x 17 cm

surface using all the tricks we learned as children while playing with bathtub water and puddles.

In addition to fluid dynamic appearances, it is also possible to obtain chemical-physical appearances of great scientific and aesthetic interest by immersing non-conductive liquid-soaked titanium in a conductive liquid. In this way, the subsequent positions of the solution's advancing front are fixed while moving the liquid away from the metal surface, bringing it into solution, mixing, or reacting chemically with it. In this case too, Nature reveals itself in a practically limitless number of forms, surpassing human imagination with its infinite possibilities. Just as Pascal claimed: "the imagination will tire of creating before nature tires of revealing itself."

Unlike field appearances where timeless landscapes predominate and color modulations organize space, those in motion tell the story of how specific hydraulic or chemical-physical processes have occurred. The chromatic discontinuities, generated by the cyclic pulsing of the potential, mark time like rhythm in music. It could be said, paraphrasing Klee, that while the former bring order to stillness, the latter bring it to motion. Field appearances and motion appearances are different and convey different sensations. However, there is one thing they do equally and equally well. They show that the hidden side of Nature they make visible is no less beautiful than what is presented daily to our eyes.

Creative moment

Sometimes, those who bring appearances to life, in addition to being the operator behind the camera, are the screenwriter and director in the sense that they first imagine the nanometric landscape defined by the potential distribution or the hydraulic or chemical-physical story to be staged. Then they make it happen on the surface of titanium (on the stage of titanium, one might say) and record its magic and evolutionary processes. The most intense moment is when, having imagined the phenomenon, one begins to produce it. This is where the state of waiting, the suspense, the secret magnetism of thresholds, passages, glimpses, and contact with the unknown begin, to use the words of Giancarlo Consonni. From this moment, a kind of creative communion occurs between the operator and the natural phenomenon, as Maria Corti writes.

The method described is not just a means of capturing, revealing, admiring, or studying a world of natural phenomena that is often otherwise invisible. It is also a tool for interacting, modifying, and playing with this world and for using it, through the resources of imagination and inventiveness, to create another world composed of forms that no longer replicate those of nature, even though they faithfully adhere to its laws. In other words, it is a designed imaginary, as Lodovico Meneghetti writes, outside the random and fantastic shapes of nature but within its phenomenal rules.

However, there is another intriguing aspect of motion appearances, related to the fact that they can only capture wavefronts in their initial transitory phenomenon but not in their permanent movements. This circumstance, as noted by Costantino Fassò, may be considered a limitation from a scientific standpoint, but from an aesthetic and emotional perspective, it gives appearances a "Faustian" dimension. It allows them to capture the splendor of the fleeting moment and thus fulfill Faust's dream, as Goethe has him say: "That I may say to the moment, "Stay, you are so beautiful!"

Other possibilities

We have focused extensively on appearances, but similar attention could be devoted to other graphic and chromatic effects that can be achieved on titanium. We will mention a few. You can apply a succession of electrical pulses between a brush moving across the surface of titanium and the surface itself to create an alternation of colors from the first and second scales. This way, the successive positions of the advancing brush are captured at the same rate as the pulses are sent. You can selectively remove the oxides and, hence, the colors from the second scale, and replace them with those from the first, achieving a kind of electrochemical "*niello*". Niello refers to the old technique used by medieval goldsmiths to create inlays on the surface of gold objects and highlight them by filling them with appropriate substances. In this case, it is electrochemical because this operation on titanium is not performed with an engraving tool but rather by exploiting an electrochemical process. You can treat colored plates with special solutions and transition from color to black and white. You can produce perfectly stable colors, or others with a programmed decay, going from the eternal to the ephemeral. Finally, you can create areas of varying roughness, or of reflection, or, conversely, opaque areas, creating the effects of depth, three-dimensionality, and with alternating white and colored lighting and more special chromatic plays.

As Consonni writes, the availability of an extraordinary material that allows for the creation of precious colors and unique forms produced by nature itself in all their compelling elegance can only be seen as a challenge to its artistic use.

Let's Talk About Titanium

Origins, production methods, costs, and applications of the on-trend metal in various areas And as for the future? No limits, especially for architects

Some myths about titanium need to be dispelled. Firstly, it is not a rare element. In the hierarchy of the most abundant metals in the Earth's crust, where it is found at a concentration of around 0.6%, titanium is surpassed only by aluminum, iron, and magnesium. It comes before widely used metals like copper, zinc, and chromium. Secondly, its discovery is not recent but dates back over two hundred years. If anything, the process that allows it to be extracted from minerals (the Kroll process) is relatively recent, from 1937, and its industrial-scale production and application only began after World War II.

Lastly, it is an expensive metal, but not exorbitantly so. The challenges associated with concentrating the starting mineral and extracting it, along with the high energy costs required to separate it from the oxygen to which it has a strong affinity, make it cost about ten times more than stainless steel today. However, if you compare it based on volume or the surface area of sheets of equal thickness, its cost is only about seven to eight times that of stainless steel because the latter's density is almost double that of titanium. For the majority of applications, this is the comparison that matters.

Titanium: Mythology and Laboratory

In 1789, the French chemist Vauquelin, while analyzing a particular mineral, rutile (TiO_2), discovered an unknown element. The same thing happened two years later to the English reverend Gregor while studying the sands of his parish's mining district in Cornwall, which is known today to be rich in ilmenite, the most common titanium mineral ($FeTiO_2$).

In 1795, the German chemist Klaproth, using sands from Hungary, also discovered this new element, demonstrated it to be the same as the one Gregor had found, and named it titanium.

There are two versions regarding the origin of the name. According to some, Klaproth drew inspiration from the Titans, the six children of Uranus (heaven) and Gaea (earth), who, according to Hesiod's account, engaged in a battle with Jupiter to conquer Mount Olympus and, after being defeated, were cast into Tartarus. According to others, Klaproth was inspired by Titania, the wife of Oberon, the king of the fairies in Nordic mythology, and a co-protagonist with her husband in Shakespeare's *A Midsummer Night's Dream.*

It wasn't util the second decade of the 20th century that significant quantities of titanium could be obtained in the laboratory. However, it was only in 1937 that Kroll developed a process that paved the way for its industrial production.

Despite numerous attempts to produce it through electrochemical methods, similar to how other metals with a strong affinity for oxygen like aluminum, magnesium, or sodium are produced, titanium is still primarily manufactured using the Kroll process. This process is not inspired by traditional metallurgical methods but rather follows the typical approach of inorganic chemistry. In a chemical reactor, titanium tetrachloride ($TiCl_4$) is prepared from the oxide and carbon. Then, in another reactor, it is made to react with magnesium. This process yields small grains of the metal, which are subsequently compacted into a sponge-like form. Only after further purification and treatment in an electric arc furnace is the metal obtained.

The various applications

Industrial production of titanium began in 1947. Since then, its applications have continued to grow and diversify. Initially, it was used exclusively in the military field, particularly in aerospace and aviation. Then, in the 1960s, it entered the chemical industry, and a few years later, the electrochemical industry. In the 1970s and 1980s, it found use in all other sectors, including mechanical, petrochemical, energy, aviation, land, and marine transportation, architectural, monument restoration, food, environmental, biomedical, sports, and leisure.

Titanium has a high melting point (1650°C), a low coefficient of thermal expansion, is non-magnetic, and remains non-brittle at low temperatures. Its mechanical strength-to-density ratio, in the range of 200-500°C, is superior to that of other metals. It can be cast, forged, welded, and machined. It is available as a pure metal and as an alloy, offering a wide range of mechanical characteristics, corrosion resistance, and surface finishes, both in its natural gray color and in the hues provided by its oxides.

Today, its applications are extremely diverse. Its mechanical strength, lightweight nature, and corrosion resistance make it suitable for use in the construction of aircraft, helicopters, submarines, and it is preferred for engine components, automotive accessories, sports equipment such as golf clubs, tennis rackets, skis, bicycles, scuba gear, as well as leisure items ranging from luxurious gardening tools to ultra-lightweight camera bodies.

Corrosion Resistance

Titanium's corrosion resistance makes it competitive in the chemical reactor and heat exchange sector. Its ability to form surface films with special electrochemical characteristics when combined with other metals, such as iridium and ruthenium, has transformed it into the perfect insoluble anode. Since the 1970s, it has revolutionized the chlor-alkali industry and made significant contributions to the development of electroplating and cathodic protection.

Its appealing appearance and resistance to atmospheric agents make it an ideal material for architectural applications, despite its relatively high price. Its low coefficient of thermal expansion and durability allow it to be paired with ceramic or stone materials, making it suitable for the restoration of architectural assets and works of art. This has already been done for several landmarks like the Parthenon, the Erechtheion, Trajan's Column, the Antonine Column, and the Trevi Fountain, to name just a few.

Its biocompatibility and mechanical strength make it essential for orthopedic prostheses, dental implants, and pacemakers. Its hypoallergenic properties, lightweight nature, strength, and attractive colors open up opportunities in the fields of eyeglass frames and jewelry.

Lastly, all the various properties listed so far, along with others such as the ability to recover previously held shapes (known as *shape memory*) and to take on vibrant and delicate colors, promote its use in the fields of design, fashion, interior decoration, and high technology. The primary method to achieve colored titanium is through electrochemical oxidation.

Titanium is indeed a metal with diverse, often extreme characteristics and multiple applications. Therefore, it should be rightfully included among the most industrially important metals.

A material so fascinating, entering the worlds of technology, art, and health, serving both for flight and for deep-sea exploration, for healing and for destruction, providing grace and strength, making dreams and turning them into reality, might be illustrated with more warmth and imagination. But perhaps that's not necessary. To appreciate titanium, the lists of its characteristics and its uses (as found in manufacturers' and sellers' metal bulletins) are enough.

However, if someone really wants to, they can add that it was titanium that took man to the moon, or that the Titanic sank because it wasn't made of titanium. Or they can have Homer or Hesiod tell the tale of the Titans' struggle for Olympus, or Shakespeare recount the story of the Queen of the Fairies, Titania, and her husband, King Oberon, who, to make her fall in love....

Architectural applications

The attractive appearance of oxidized titanium and its resistance to weathering have opened up the architectural sector to this material. The majority of applications are in Japan and involve roofing, external and internal cladding of significant buildings.

In Italy, there are no significant architectural works that use colored titanium. However, Marco Dezzi Bardeschi has envisaged its use to emphasize the steel structure of the emergency staircase of the medieval Palazzo della Ragione, located in the center of the Broletto in Milan.

Titanium is often used in its *natural* color, which can resemble, at first glance, that of iron or stainless steel. However, in some of its finishes, the metal's surface reflects colored highlights with shades that change depending on the viewing angle and the type of lighting.

For example, it can appear yellow in the morning, gray when the sun is not shining, pink at sunset, blue at night, or exhibit iridescent and multicolored flashes under artificial lighting. This behavior is well illustrated by the Guggenheim Museum in Bilbao, inaugurated in 1998, where the Californian architect Frank O. Gehry has created an *astonishing titanium shell* with a particular *natural* gray finish. François Burkhardt writes, "A sort of large metal band wraps around the various *boxes* that make up the museum, ensuring their unity and forming a believable *landscape*. With its multitude of sloping and rounded surfaces, it transports light, making it different in color at every point, ultimately creating a highly effective monochromatic effect ranging from gold to blue and from pink to white."

Perhaps, beyond the beauty of colors and reflections, it is fascinating to think that properly prepared titanium surfaces, not subject to abrasion, will preserve their beauty over time. In an era where the life of a reinforced concrete structure - the common building material of our days - is measured more in decades than centuries, titanium gives architects the certainty that they can erect significant monuments - "taller than the royal moles of the pyramids" - that "neither acid rains, nor polluted atmospheres, nor the unrestrained north wind can destroy, nor the inexorable passing of years and the flight of time."

In other words, monuments "more enduring than bronze," if it is permissible to paraphrase Horace's verses to an engineer who is not Gadda.

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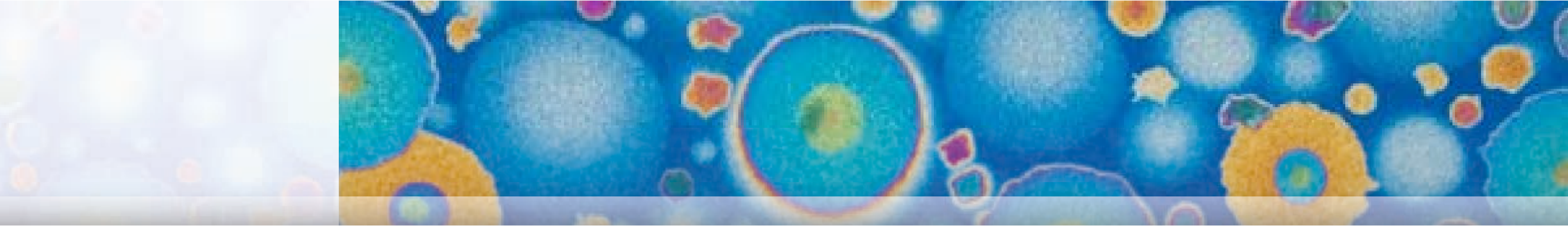

Pietro Pedeferri

Tales of corrosion (and other stories)

This volume is a collection of some of the popular science publications, *Tales of Corrosion* (Storie di Corrosione), written by Pietro Pedeferri over the course of his life. In these readings, corrosion is the common thread that connects his work as a scientist and engineer to that of a teacher and artist. The readings narrate episodes from his life, experiences related to his profession as a university professor and an expert in the durability of metallic materials, and his life as a titanium artist.

Pietro Pedeferri, born in Valtellina, graduated in Chemical Engineering from the Politecnico di Milano in 1963. He became a full professor infirst in "Electrochemistry" and later in "Corrosion and Materials Protection." He was a member of the Board of Directors and the Academic Senate of Politecnico di Milano. Additionally, he served as Head of Department and was a full member of the Lombard Institute Academy of Sciences and Letters. Pedeferri made significant scientific contributions to corrosion, both in terms of theoretical aspects and corrosion engineering. From the late 1970s, he devoted himself with artistic sensitivity and scientific rigor to the oxidation of titanium, achieving extraordinary and surprising chromatic effects.